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CHEMISTRY

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CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 34

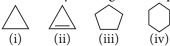
JEE MAIN/PMTs

1. Identify the compound '*B*' in the following reaction sequence.

$$\begin{array}{c} \text{CH}_2(\text{COOC}_2\text{H}_5)_2 \xrightarrow{\text{NaOEt}} (A) \xrightarrow{\text{CH}_3\text{CHBrCOOC}_2\text{H}_5} (B) \\ & \xrightarrow{\text{H}_3\text{O}^+} \Delta \\ \text{CH}_3 - \text{CH} - \text{COOH} \longleftarrow \\ \text{CH}_2 - \text{COOH} \end{array}$$

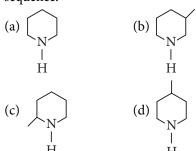
- $\begin{array}{c} \operatorname{COOC_2H_5} \\ \text{(a)} \quad \operatorname{CH-CH}(\operatorname{COOC_2H_5})_2 \\ \operatorname{CH_3} \end{array}$
- $\begin{array}{c} \operatorname{COOH} \\ \mid \\ \operatorname{CH-CH_2-COOH} \\ \vdash \\ \operatorname{CH_3} \end{array}$
- $\begin{array}{c} \operatorname{COOC_2H_5} \\ | \\ \operatorname{CH-CH_2-COOH} \\ | \\ \operatorname{CH_3} \end{array}$
- $\begin{array}{c} {\rm COOH} \\ ({\rm d}) \ {\rm CH-CH(COOC_2H_5)_2} \\ {\rm CH_3} \end{array}$
- 2. At 3 km altitude, water boils at 90°C and 300 seconds are taken to cook a '3 minute egg'. The temperature coefficient for the process of cooking is
 - (a) 2.66
- (b) 1.66
- (c) 3.66
- (d) 0.6

3. The order of stability of the given compounds is



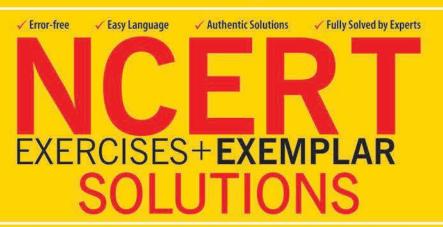
- (a) (iv) > (iii) > (i) > (ii)
- (b) (i) > (iii) > (ii) > (iv)
- (c) (ii) > (iii) > (i) > (iv)
- (d) (iv) > (i) > (iii) > (ii)
- 4. $X \xrightarrow{\text{CH}_3\text{I}} Y \xrightarrow{\text{CH}_3\text{I}} Y \xrightarrow{\text{CH}_3\text{I}} |$

Identify the compound X in the above reaction sequence.



- **5.** Which one of the following statements does not govern the second law of thermodynamics?
 - (a) Total entropy of the universe is continuously increasing.
 - (b) Entropy of a perfectly crystalline solid at absolute zero is taken as zero.
 - (c) Without the help of an external agency, a spontaneous process cannot be reversed.
 - (d) All naturally occurring processes are irreversible.

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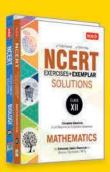












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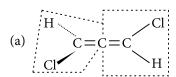
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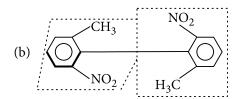


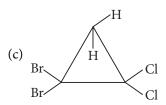
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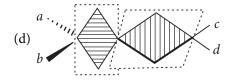
JEE ADVANCED

6. Which one of the following does not show optical activity?









COMPREHENSION

A powdered substance (*A*) on treatment with fusion mixture gives a green coloured compound (B). The compound (B) on acidification with dilute H2SO4 gives a pink coloured compound (C). When (A) is treated with excess of NaOH and bromine water, (D) is obtained. Solution of (A) in dilute HCl on treatment with a solution of barium chloride gave a white precipitate of (E), which was insoluble in conc. HNO3 and conc. HCl.

- **7.** Green coloured compound (*B*) is
 - (a) Na_2MnO_4
- (b) MnO₂
- (c) BaCl₂
- (d) NaMnO₄
- **8.** The compound (D) is
 - (a) MnSO₄
- (b) Na₂MnO₄
- (c) MnO₂
- (d) BaSO₄

INTEGER VALUE

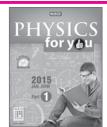
9. The total number of inner-orbital complexes among the following is

$$\begin{split} & [\text{Pt}(\text{NH}_3)_6]^{4^+} \,, \, [\text{Ni}(\text{H}_2\text{O})_6]^{2^+} \,, \, [\text{Fe}(\text{CN})_6]^{4^-}, \\ & [\text{Fe}(\text{H}_2\text{O})_6]^{3^+} \,, \, [\text{Co}(\text{CN})_6]^{3^-} \,, \, [\text{Ir}(\text{NH}_3)_6]^{3^+} \,, \, [\text{CoF}_6]^{3^-} \end{split}$$

10. 0.553 g of a boron-hydrogen compound (B_xH_y) created a pressure of 0.658 atm in a bulb of 407 mL at 100°C. Analysis showed the compound contains 85.7% boron. In the molecular formula B_xH_y , y is (Given : At. wt. of B = 10.8 u).



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JEE ADVANCED PRACTICE PAPER

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PAPER-I

SECTION-1

- This section contains EIGHT questions
- The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, both inclusive
- 1. A certain mass of a substance when dissolved in 100 g C_6H_6 lowers the freezing point by 1.28 °C. The same mass of solute when dissolved in 100 g of water lowers the freezing point by 1.40 °C. If the substance has normal molecular mass in benzene and is completely dissociated in water, the number of ions formed when it dissociates in water is $[K_f \text{ for } H_2\text{O} \text{ and } C_6H_6 \text{ are } 1.86 \text{ and } 5.12 \text{ K mol}^{-1} \text{ kg respectively}].$
- **2.** A molecule of the type AX_5 has square pyramidal geometry. Hence, number of lone pairs on A is
- **3.** The percentage ionic character of the HBr molecule if the dipole moment is 0.63 D and HBr bond length 187.5 pm is
- **4.** Ethylenediamine displaces H_2O in the complex $[Fe(H_2O)_6]^{3+}$ in three steps. $[Fe(H_2O)_6]^{3+} + 3en \longrightarrow [Fe(en)_3]^{3+} + 6H_2O$ Stepwise formation constant are

 $\log K_1 = 4.34$; $\log K_2 = 3.31$; $\log K_3 = 2.05$ Overall formation constant is $A \times 10^B$ where the value of A is

- **5.** In the Bohr's model of the hydrogen atom, the ratio of the kinetic energy to the total energy of the electron in a quantum state n is -x, where x is
- **6.** The value of K_c for the following reaction at 25 °C is 2.63×10^x .

$$Cu_{(aq)}^{2+} + Sn_{(aq)}^{2+} \longrightarrow Sn_{(aq)}^{4+} + Cu_{(s)}$$

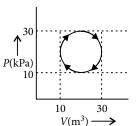
 $E_{Cu^{2+}/Cu}^{\circ} = 0.34 \text{ volt}, E_{Sn^{4+}/Sn^{2+}}^{\circ} = 0.15 \text{ volt}$
The value of x is

- 7. The number of optical isomers for the compound [CH(OH)COOH]₂ is
- **8.** Amongst the following, the total number of compounds soluble in aqueous NaOH is

SECTION-2

- This section contains TEN questions
- Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct
- 9. The melting point of RbBr is 682°C while that of NaF is 988°C. The principal reason that the melting point of NaF is much higher than that of RbBr is that
 - (a) the two crystals are not isomorphous
 - (b) the molar mass of NaF is smaller than that of RbBr
 - (c) the bond in RbBr has more covalent character than the bond in NaF
 - (d) the internuclear distance $(r_c + r_a)$ is greater for RbBr than for NaF.
- **10.** Which is/are not the true statement(s) about $KMnO_4$?

- (a) Its solution is unstable in acidic medium.
- (b) It gets reduced to MnO₂ in neutral medium.
- (c) MnO₄ changes to Mn²⁺ in basic solution.
- (d) It is self-indicator in Fe^{2+} or $C_2O_4^{2-}$ titration.
- 11. Which of the following easily undergo(es) nucleophilic substitution by S_N1 mechanism in butanol?
 - (a) $C_6H_5CH_2Br$
- (b) BrCH₂CH=CH₂
- (c) $(CH_3)_3CBr$
- (d) (CH₃)₃CCH₂Br
- **12.** Extraction of metal from the ore cassiterite involves
 - (a) carbon reduction of an oxide ore
 - (b) self-reduction of a sulphide ore
 - (c) removal of copper impurity
 - (d) removal of iron impurity.
- 13. Which of the following is/are correct for a cyclic process as shown in the figure?



(a)
$$dU = 0$$

(b)
$$q = -w$$

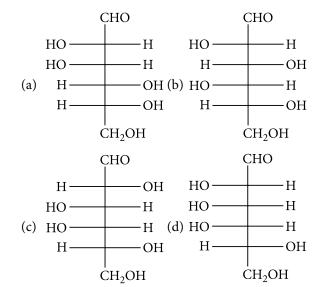
(c)
$$w = 314 \text{ J}$$

(d)
$$w = 31.4 \text{ J}$$

- **14.** Which of the following statements is/are correct about HCOOH?
 - (a) It is a stronger acid than CH₃COOH.
 - (b) It forms formyl chloride with PCl₅.
 - (c) It gives CO and H_2O on heating with conc. H_2SO_4 .
 - (d) It reduces Tollens' reagent.
- 15. End product(s) of the following reaction is/are

(a)
$$\frac{\text{conc. H}_2SO_4}{\text{Heat}}$$
(b) $\frac{\text{conc. H}_2SO_4}{\text{Heat}}$

16. Which of the following monosaccharides yield(s) an optically active alditol on NaBH₄ reduction?



- 17. To an acidic solution of an anion, a few drops of KMnO₄ solution are added. Which of the following, if present, will not decolourise the KMnO₄ solution?
 - (a) CO_3^{2-}
- (b) NO_2^-
- (c) S^{2-}
- (d) Cl⁻
- 18. Pure ammonia is placed in a vessel at a temperature when its dissociation constant (α) is appreciable. At equilibrium,
 - (a) K_p does not change significantly with pressure
 - (b) α does not change with pressure
 - (c) concentration of NH₃ does not change with
 - (d) concentration of H_2 is less than that of N_2 .

SECTION-3

- This section contains TWO questions
- Each question contains two columns, Column I and Column II
- Column I has four entries (A), (B), (C) and (D).
- Column II has four entries (P), (Q), (R) and (S).
- Match the entries in Column I with the entries in Column II
- One or more entries in Column I may match with one or more entries in Column II
- **19.** Match the entries listed in Column I with appropriate entries listed in Column II.

Column I

Column II

- (A) Poling
- (P) Titanium
- (B) Cupellation
- (Q) Copper
- (C) Electrorefining
- (R) Silver
- (D) van Arkel method
- (S) Tin

20. Match the entries listed in Column I with appropriate entries listed in Column II.

Column I

(A)
$$\stackrel{\text{O}}{\longrightarrow} \frac{\text{NaCN} + \text{H}_2\text{SO}_4}{\longrightarrow} (X) \xrightarrow{\text{LiAlH}_4} (Y) \xrightarrow{\text{HNO}_2} (Z)$$

(B)
$$NH_2OH \rightarrow (X) \xrightarrow{H^+} (Y) \xrightarrow{LiAlH_4} (Z)$$

(C)
$$CH_3$$
- C - CH_2 - CH_2 - CH_2 - C - H - Δ Product O

(D)
$$CH_3 \xrightarrow{H^+} Product$$

Column II

- (P) Formation of six membered ring takes place
- (Q) Final product is a ketone
- (R) Final product formed will give positive Tollens' test
- (S) Final product will react with 2, 4-DNP
- (T) Final product have 5 membered ring

PAPER-II

SECTION-1

- This section contains EIGHT questions
- The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, both inclusive
- 1. The first and second dissociation constant of H_2S are 1×10^{-7} and 1.3×10^{-14} respectively. Then the approximate pH of a 0.1 M $H_2S_{(aq)}$ solution is
- 2. The number of possible isomers of the complex, $Pt(NH_3)_2(SCN)_2$ are
- 3. A 1.1 g sample of copper ore is dissolved and Cu²⁺_(aq) is titrated with excess KI. The liberated I₂ requires 12.12 mL of 0.1 M Na₂S₂O₃ solution for its titration. The percentage of copper by mass in the ore is
- 4. $MCl_4 \xrightarrow{(i) Zn} (B)$ purple colour compound

Colourless liquid at room temperature,

transition metal

Moist air

White fumes (*C*)

The number of unpaired electrons in the compound (*B*) is

 Amongst the following, total number of compounds soluble in sodium bicarbonate is
 4, 6-trinitrophenol, benzoic acid, salicylic acid, trifluoroethanol, acetamide, benzenesulphonic acid

- 6. In a sample of pitchblende the ratio of $^{206}\text{Pb}:^{238}\text{U} = 0.2:1$ by weight. If the disintegration constant of ^{238}U is 1.54×10^{-10} per year and all Pb is supposed to be originated from uranium then, the age of the mineral is 1.35×10^x years. The value of x is
- 7. Oxidation number of Cr in the following complex is $\frac{1}{2}$

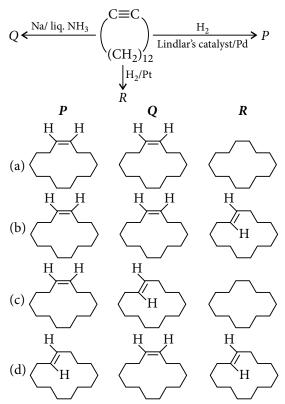
$$\left[(H_2O)_6Cr \stackrel{O_2}{<} Cr(H_2O)_6 \right]^3$$

8. In the given list the number of compounds which cannot show tautomerism is acetophenone, acetaldehyde, cyclohexanone, acetylacetone, benzoquinone, acetone, benzaldehyde, butanone, ethyl acetoacetate

SECTION-2

- This section contains EIGHT questions
- Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct
- 9. The pressure in a bulb dropped from 2000 mm to 1500 mm of Hg in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio 1: 1 at a total pressure of 4000 mm of Hg was introduced. The molar ratio of the two gases remaining in the bulb after a period of 74 minutes is
 - (a) 0.8089:1
- (b) 1:0.8089
- (c) 1:0.1499
- (d) 0.1499:1

10. What are *P*, *Q* and *R* in the following reactions?



- 11. A colourless mixture of two compounds 'A' and ('B' in excess) is soluble in H₂O. 'A' turns blue litmus red and 'B' turns red litmus blue. 'A' gives white precipitate with 'B' which dissolves in excess of 'B' forming 'C'. 'A' when placed in atmosphere gives fumes and can form dimer. 'A' gives white precipitate with NH₄Cl and NH₄OH soluble in 'B'. 'A', 'B' and 'C' are respectively
 - (a) AgCl, KOH and KCl
 - (b) AlCl₃, NaOH and NaAlO₂
 - (c) PbCl₂, KOH and Al(OH)₃
 - (d) MgCl₂, NaH, and NaAlO₂
- **12.** Which of the following statements is/are correct about the electrophilic substitution reactions in given compounds *A* and *B*?

$$\begin{array}{c|c}
O & O \\
C & O \\
A
\end{array}$$

$$\begin{array}{c|c}
O & O \\
C & O \\
C & O
\end{array}$$

$$\begin{array}{c|c}
O & O \\
C & O \\
B
\end{array}$$

- (a) Compound *A* is more reactive than compound *B*.
- (b) In A, ring Y will take part in electrophilic substitution reaction.

- (c) In *B*, ring *Q* will take part in electrophilic substitution reaction.
- (d) Compound *B* is more reactive than compound *A*.
- 13. In the reaction: $2X + B_2H_6 \longrightarrow [BH_2(X)_2]^+[BH_4]^-$, the amine(s) X is(are)
 - (a) NH₃
- (b) CH₃NH₂
- (c) (CH₃)₂NH
- (d) (CH₃)₃N
- 14. The compound

$$R_1 > N - R_3$$

forms nitroso amines when the substituents are

- (a) $R_1 = CH_3$, $R_2 = R_3 = H$
- (b) $R_1 = R_2 = H$, $R_3 = C_2H_5$
- (c) $R_1 = H$, $R_2 = R_3 = CH_3$
- (d) $R_1 = CH_3$, $R_2 = C_2H_5$, $R_3 = CH_3$
- **15.** Which of the following statement(s) is/are not correct?
 - (a) All C—O bonds in CO_3^{2-} are equal but not in H_2CO_3 .
 - (b) All C-O bonds in HCO $_2^-$ are equal but not in HCO $_2$ H.
 - (c) C-O bond length in HCO $_2^-$ is longer than C-O bond length in CO $_3^{2-}$.
 - (d) C—O bond length in HCO_2^- and C—O bond length in CO_3^{2-} are equal.
- **16.** A gas obeys P(V b) = RT. Which of the following statement(s) is/are correct about this gas?
 - (a) Isochoric curves have slope = $\frac{R}{V-h}$.
 - (b) Isobaric curves have slope = $\frac{R}{P}$ and intercept = b.
 - (c) For the gas, compressibility factor = $1 + \frac{Pb}{RT}$.
 - (d) The attractive forces are overcome by repulsive forces.

SECTION-3

- This section contains TWO paragraphs
- Based on each paragraph, there will be TWO questions
- Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct

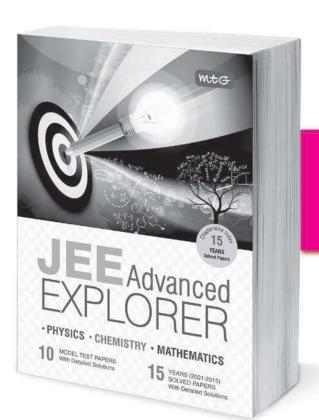
PARAGRAPH 1

Concrete is produced from a mixture of cement, water and small stones. Small amount of gypsum, CaSO₄·2H₂O is added in cement production to improve the subsequent hardening of concrete. The elevated temperature during the production of cement

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may lead to the formation of unwanted hemihydrate $CaSO_4 \cdot \frac{1}{2}H_2O$ according to reaction :

$$CaSO_4 \cdot 2H_2O_{(s)} \longrightarrow CaSO_4 \cdot \frac{1}{2}H_2O_{(s)} + \frac{3}{2}H_2O_{(g)}$$

The $\Delta_f H^\circ$ of CaSO₄·2H₂O_(s), CaSO₄· $\frac{1}{2}$ H₂O_(s), H₂O_(g) are -2021.0 kJ mol⁻¹, -1575.0 kJ mol⁻¹, and -241.8 kJ mol⁻¹ respectively. The respective values of their standard entropies are 194.0, 130.0 and 188.0 J K⁻¹ mol⁻¹. The values of R = 8.314 J K⁻¹ mol⁻¹ = 0.0831 L bar mol⁻¹ K⁻¹.

17. Heat change occurring during conversion of 1 kg of $CaSO_4 \cdot 2H_2O_{(s)}$ (molar mass 172 g mol⁻¹) to

$$CaSO_4 \cdot \frac{1}{2} H_2 O_{(s)}$$
 is

- (a) 484 kJ
- (b) 400 kJ
- (c) -484.0 kJ
- (d) -1000 kJ
- **18.** The formation of $CaSO_4 \cdot \frac{1}{2}H_2O$ at 298 K is
 - (a) spontaneous
 - (b) endothermic and non-spontaneous
 - (c) endothermic and spontaneous
 - (d) exothermic and non-spontaneous.

PARAGRAPH 2

 $S_{\rm N}^2$ reaction is bimolecular reaction which takes place by the formation of transition state. Velocity of the reaction depends on the concentration of the substrate as well as the nucleophile. The reaction is favoured by strong nucleophile and in the presence of polar aprotic solvent, optically active halides undergo Walden inversion by $S_{\rm N}^2$ mechanism. The presence of hetero group (atom) at

 β C-atom, unsaturation at β C-atom and C group at α C-atom favour S_N^2 mechanism.

Allyl halides and benzyl halides give $S_N 1$ and $S_N 2$ reactions. Allyl halides also give $S_N 2$ mechanism. Electron donating group at *ortho-* and *para-*positions in benzyl halides favours $S_N 1$ mechanism, whereas electron withdrawing group favours $S_N 2$ mechanism.

- **19.** Which of the following will give S_N2 reaction
 - (a) C_2H_5Br
- (b) CH₃Br

(d)
$$Me_3C$$
— CH_2B_2

- 20. In the reaction $\underset{\text{Me}}{\text{Br}} \xrightarrow{\text{O}} \xrightarrow{\text{HOH}} [X], [X] \text{ is}$
 - (a) C_2H_5Br
- (b) Me COOAg
- (c) Me
- (d) $CH_2 = CH_2$

SOLUTIONS

PAPER-I

1. (3):
$$\Delta T_f = \frac{1000 \times K_f \times w_2}{M_2 \times w_{1(\text{in g})}}$$

For the solution in benzene,

$$1.28 = \frac{1000 \times 5.12 \times w_2}{M_{\text{normal}} \times 100} \qquad \dots (i)$$

For the solution in water in which solute dissociates,

1.40 =
$$\frac{1000 \times 1.86 \times w_2}{M_{\text{experimental}} \times 100}$$
 ...(ii)

Dividing eq. (ii) by (i),

$$i = \frac{M_{\text{normal}}}{M_{\text{experimental}}} = \frac{1.40}{1.28} \times \frac{5.12}{1.86} = 3.01 \approx 3.0$$

Now, suppose that formula of the solute is $A_x B_v$.

$$\begin{array}{ccc}
A_x B_y & \longrightarrow xA^+ + yB^- \\
1 & 0 & 0 \\
(1 - \alpha) & x\alpha & y\alpha
\end{array}$$

- $\therefore \quad i = 1 \alpha + x\alpha + y\alpha$
- i = 3 and $\alpha = 1$ (Given that $\alpha = 1$)
- \therefore No. of ions formed (x + y) = 3
- 2. (1): Square pyramidal geometry sp^3d^2 hybridisation of central atom with 5 bond pairs and 1 lone pair.
- 3. (7): Calculated value of $\mu = e \times l$

$$= 4.8 \times 10^{-10} \text{ esu} \times 187.5 \times 10^{-10} \text{ cm}$$

$$= 9 \times 10^{-18}$$
 esu cm

= 9 Debye
$$(1 \times 10^{-18} \text{ esu cm} = 1 \text{ Debye})$$

Observed value of $\mu = 0.63$ Debye

% ionic character =
$$\frac{\text{observed value} \times 100}{\text{calculated value}}$$

= $\frac{0.63}{9} \times 100 = 7\%$

4. (5): $[Fe(H_2O)_6]^{3+} + 3en \longrightarrow [Fe(en)_3]^{3+} + 6H_2O$

$$\beta_3 = \frac{[\text{Fe}(en)_3]^{3+}}{[\text{Fe}(\text{H}_2\text{O})_6]^{3+}[en]^3} = K_1 \times K_2 \times K_3$$

$$\Rightarrow \log \beta_3 = \log K_1 + \log K_2 + \log K_3$$

As
$$\log K_1 = 4.34$$
, $\log K_2 = 3.31$, $\log K_3 = 2.05$

$$\therefore \log \beta_3 = 4.34 + 3.31 + 2.05 = 9.7$$

$$\beta_3 = 5 \times 10^9 \text{ hence, } A \text{ is 5.}$$

5. (1): *K.E.* of an electron in an orbit =
$$+\frac{1}{2}\frac{e^2}{r_n}$$

Total energy of an electron in an orbit =
$$-\frac{e^2}{2r_n}$$

 $\frac{K.E.}{T.E} = -1$ thus, $x = 1$

6. (6): The cell may be represented as
$$\operatorname{Sn}^{2+} | \operatorname{Sn}^{4+} | | \operatorname{Cu}^{2+} | \operatorname{Cu}$$

To calculate K_c , the cell reaction should be at equilibrium, *i.e.*, $E_{\text{cell}} = 0$

$$E_{\text{cell}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Sn}^{4+}/\text{Sn}^{2+}} = 0$$

or
$$\left\{E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} + \frac{0.0591}{2}\log[\text{Cu}^{2+}]\right\} - \left\{E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ} + \frac{0.0591}{2}\log\frac{[\text{Sn}^{4+}]}{[\text{Sn}^{2+}]}\right\} = 0$$

or
$$\left\{E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ}\right\} + \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}][\text{Sn}^{2+}]}{[\text{Sn}^{4+}]} = 0$$

or
$$(+0.34-0.15) - \frac{0.0591}{2} \log \frac{[Sn^{4+}]}{[Cu^{2+}][Sn^{2+}]} = 0$$

or
$$0.19 - \frac{0.0591}{2} \log K_c = 0$$

or
$$\log K_c = 6.42$$

or
$$K_c = 2.69 \times 10^6$$

7. (3): The structure of the compound can also be written as

No. of asymmetric C atoms $(C^*) = 2$ but the two ends are similar or the molecule is divisible into equal halves.

Hence, No. of *d*- and *l*-forms,

$$a = 2^{n-1} = 2^{2-1} = 2$$

No. of meso-forms,

$$m = 2^{\frac{n}{2} - 1} = 2^{\frac{2}{2} - 1} = 2^{0} = 1$$

No. of optical isomers = a + m = 2 + 1 = 3

8. (4): Out of the given compounds, those soluble in aq. NaOH are:

COOH OH OH COOH
$$\begin{array}{c}
\text{COOH} \\
\text{N}
\end{array}$$

$$\begin{array}{c}
\text{H}_{3}\text{C} \\
\text{CH}_{3}
\end{array}$$

9. (d): The melting point of a crystal is directly proportional to its lattice energy. The lattice energy in case of ionic crystals is itself dependent on the charge of the particles and the distance between them *i.e.*, the bond length.

Lattice energy
$$\propto \frac{1}{r_c + r_a}$$

The charge in case of NaF as well as RbBr is the same but the bond length in case of RbBr is much more than NaF. Hence, the melting point of NaF is much higher than RbBr.

- 10. (c): MnO_4^- changes to MnO_4^{2-} or MnO_2 in basic medium.
- 11. (a, b, c, d): All form stable carbocations therefore, all options are correct.
 - (a) $C_6H_5\overset{\text{T}}{C}H_2$ is stabilised by resonance over the phenyl ring
 - (b) $CH_2 = CH CH_2 \leftrightarrow CH_2 CH = CH_2$ is also stabilised by resonance.

(c)
$$CH_3 \rightarrow \overset{\uparrow}{C} \leftarrow CH_3$$

 CH_3

is stabilised by +I-effect of $-CH_3$ groups.

(d)
$$CH_3 - C - CH_2 \xrightarrow{P} Br \xrightarrow{Ionisation} CH_3$$

Neopentyl bromide

$$\begin{array}{c} CH_3 & CH_3 \\ CH_3 - C - CH_2 \xrightarrow{\text{Rearranges}} CH_3 - C - CH_2 - CH_3 \\ CH_3 & 3^{\circ} \text{ carbocation} \\ \text{(less stable)} \end{array}$$

12. (a, c, d): Tin is extracted from cassiterite ore. It is reduced by carbon.

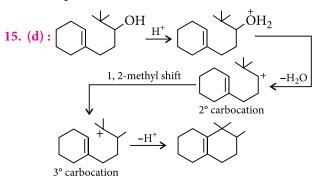
$$SnO_2 + 2C \longrightarrow Sn + 2CO$$

Crude metal contains impurities Fe, W and Cu.

- **13.** (a, b, c) : For a cyclic process, dU = 0 \therefore $q = dU + (-w) \Rightarrow q = -w$
 - Also, w =Area covered by the curve

$$= \pi r^{2} = \pi \times \left[\frac{(V_{2} - V_{1})}{2} \right]^{2}$$
$$= \frac{\pi \times (20)^{2}}{2^{2}}$$
$$= 100 \pi = 100 \times 3.14 = 314 \text{ J}$$

14. (**a**, **c**, **d**) : Formyl chloride being unstable decomposes to form CO + HCl



- **16.** (a, b, d): Only the alditol (monosaccharide having -CH₂OH at both ends) from structure (c) has a plane of symmetry hence, it will be optically inactive. The other three form optically active alditols.
- 17. (a): Oxidation state of C in CO_3^{2-} is +4, which is maximum. So, it will not be oxidised.
- **18.** (a): K_p is constant and does not change with pressure.
- 19. $A \rightarrow Q$, S; $B \rightarrow R$; $C \rightarrow Q$, R, S; $D \rightarrow P$
 - (A) Poling: Impure molten metal is stirred with green wooden poles, oxide impurities are removed, mainly used for Cu and Sn.
 - **(B)** Cupellation: It is used when impurities are of other metals, mainly used for silver.
 - (C) Electrorefining: Cu, Ag, Au, Al, Pb, Sn, etc., are mainly purified by removing insoluble impurities as anode mud.
 - (D) van Arkel method (vapour phase refining): Metals like titanium, zirconium and silicon are purified by this method.
- 20. $A \rightarrow P$, Q, S; $B \rightarrow P$, $C \rightarrow P$, Q, S; $D \rightarrow P$, Q, S

(A)
$$(X)$$
 (Y) (X) (Y) (X) (X) (X)

(B)
$$(X)$$
 (Beckmann rearrangement) (X) (C) (Y) (Y)

PAPER-II

(4): Most of the H⁺ ions result from primary dissociation, i.e.,

$$H_2S \rightleftharpoons H^+ + HS^-$$

Let x be the concentration of $[H^+]$ or $[HS^-]$ at equilibrium.

CH₃ (Pinacol-pinacolone rearrangement)

$$\therefore [H_2S] = 0.1 - x \approx 0.1 \qquad (\because x \text{ is very small.})$$

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]}$$

or
$$1 \times 10^{-7} = \frac{x \cdot x}{0.1}$$
 $\Rightarrow x^2 = 1 \times 10^{-8}$

or
$$x = 1 \times 10^{-4}$$

or
$$[H^+] = 1 \times 10^{-4}$$

$$\therefore$$
 pH = $-\log[H^+] = -\log(10^{-4}) = 4$

(6): $[Pt(NH_3)_2(SCN)_2]$ - cis and trans-isomers = 2 $[Pt(NH_3)_2(NCS)(SCN)]$ - cis and trans-isomers = 2 $[Pt(NH_3)_2(NCS)_2]$ - cis and trans-isomers = 2 The complex is square planar; so it does not have a pair of enantiomers on account of the presence of plane of symmetry.

3. (7):
$$2Cu^{2+} + 4I^{-} \longrightarrow Cu_{2}I_{2} + I_{2}$$

 $I_{2} + 2S_{2}O_{3}^{2-} \longrightarrow S_{4}O_{6}^{2-} + 2I^{-}$
 $2S_{2}O_{3}^{2-} \equiv I_{2} \equiv 2Cu^{2+}$
or $S_{2}O_{3}^{2-} \equiv Cu^{2+}$

Equivalents of $Na_2S_2O_3$ = Equivalents of I_2 = Equivalents of Cu²⁺

$$W_{\text{(Pure Cu)}} = \frac{0.1 \times 63.5 \times 12.12}{1000} = 0.077 \text{ g}$$

% of Cu = $\frac{0.077}{1.1} \times 100 = 7\%$

4. (1): (A) is TiCl₄ as it has no unpaired electron and is liquid at room temperature on account of covalent character because of high polarising power of Ti⁴⁺· TiCl₄ being covalent gets hydrolysed forming $TiO_2 \cdot nH_2O$ and HCl(C) which fumes in air. In [Ti(H₂O)₆]Cl₃ complex, Ti(III) has one unpaired electron (3d1) which gives violet or purple colour due to d – d transition.

due to
$$a - a$$
 transition.

TiCl₄ \xrightarrow{Zn} TiCl₃ $\xrightarrow{Hydrolysis}$ $\xrightarrow{H_2O}$ [Ti(H₂O)₆]Cl₃

Purple or violet

(B)

Moist air

TiO₂· n H₂O + HCl (white fumes)

- **5. (4):** Four compounds *i.e.*, 2, 4, 6-trinitrophenol, benzoic acid, salicylic acid and benzenesulphonic acid decompose NaHCO3 and hence dissolve in it.
- $^{238}U \longrightarrow ^{206}Pb$ (9): Initial moles: Moles after time t: (a - x) $\frac{\text{wt. of }^{206}\text{Pb}}{\text{wt. of }^{238}\text{U}} = \frac{0.2}{1}$ $\therefore \frac{\text{moles of Pb}^{206}}{\text{moles of U}^{238}} = \frac{0.2/206}{1/238} = \frac{0.231}{1}$ or $\frac{x}{a-x} = 0.231$ Add 1 to both sides, $1 + \frac{x}{a - x} = 0.231 + 1 \implies \frac{a}{a - x} = 1.231$ Now $\lambda = \frac{2.303}{t} \log \frac{a}{a-x}$ $\Rightarrow 1.54 \times 10^{-10} = \frac{2.303}{t} \log 1.231$ $t = 1.35 \times 10^9 \text{ years}$ $\therefore x = 9$

7. (3):
$$\left[(H_2O)_6 Cr < O_{-O_{-1}-1}^{-1} (Superoxide) \\ Cr (H_2O)_6 \right]^{3+}$$
Peroxide

Thus, oxidation state of Cr = 2x - 1 + (-2) = +3x = +3

- 8. (2): Benzoquinone and benzaldehyde cannot show tautomerism.
- **9.** (a): Suppose p_{O_2} and p_x be the pressure-drops per minute of O_2 and the unknown gas x respectively.

$$p_{O_2} = \frac{2000 - 1500}{47} = 10.64 \text{ mm/min.}$$

$$\frac{r_{O_2}}{r_x} = \frac{p_{O_2}}{p_x} = \sqrt{\frac{M_x}{M_{O_2}}}$$

$$\frac{10.64}{p_x} = \sqrt{\frac{79}{32}}; p_x = 6.77 \text{ mm/min.}$$

Since the bulb is now refilled with equal number of moles of O_2 and x, the partial pressure of each gas will be 2000 mm as the total pressure is 4000 mm.

pressure of O₂ after 74 min

= partial pressure of O_2 – pressure drop in 74 min $= 2000 - (10.64 \times 74) = 1212.64 \text{ mm of Hg}$

and pressure of x after 74 min

= partial pressure of x – pressure drop after 74 min $= 2000 - (6.77 \times 74) = 1499.02 \text{ mm of Hg}$

Moles of O₂ left after 74 min

Moles of x left after 74 min

$$= \frac{\text{Pressure of O}_2 \text{ after 74 min}}{\text{Pressure of } x \text{ after 74 min}}$$

$$= \frac{1212.64}{1499.02} - = 0.8089$$

Hence, molar ratio of O_2 and x after 74 minutes is 0.8089:1.

10. (c)

11. (b): 'A' gives white ppt. with NH₄Cl and NH₄OH 'A' is Al^{3+} and ppt. is of $Al(OH)_3$. $Al(OH)_3$ is soluble in 'B' therefore, 'B' is NaOH and 'C' is NaAlO₂ (sodium meta-aluminate). 'A' forms dimer indicating 'A' is electron-deficient that is the possible case of AlCl₃. 'A' is thus AlCl₃ (acidic due to hydrolysis, turns blue litmus red).

'B' is NaOH (alkaline, turns red litmus blue).

$$\begin{array}{c} \text{AlCl}_3 + 3\text{NaOH} \longrightarrow \text{Al(OH)}_3 + 3\text{NaCl} \\ \text{(A)} \qquad \text{(B)} \qquad \text{white ppt.} \\ \text{Al(OH)}_3 + \text{NaOH} \longrightarrow \text{NaAlO}_2 + 2\text{H}_2\text{O} \\ \text{(excess)} \qquad \text{soluble (C)} \\ \text{AlCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Al(OH)}_3 + 3\text{HCl} \uparrow \text{(fumes)} \\ \text{AlCl}_3 + 3\text{NH}_4\text{OH} \xrightarrow{\text{NH}_4\text{Cl}} \rightarrow \text{Al(OH)}_3 \downarrow + 3\text{NH}_4\text{Cl} \\ \text{2AlCl}_3 \longrightarrow \text{Al}_2\text{Cl}_6 \\ & \xrightarrow{\text{Cl}} \text{Al} \xrightarrow{\text{Cl}} \text{Al} \xrightarrow{\text{Cl}} \end{array}$$

12. (b, c, d): In compound A, ring Y is both activated and deactivated while ring X is only deactivated, hence, Yismore electron richthan X and electrophilic substitution takes place on Y ring. In compound B, ring Q is both activated and deactivated while ring *P* is only deactivated hence, *Q* will take part in electrophilic substitution reactions.

In *B*, ring *Q* is attached to N.

In *A*, ring *Y* is attached to O.

 \ddot{N} group is a stronger +R group than $-\ddot{O}$.

Hence, compound B is more reactive than compound A.

13. (a, b, c): B₂H₆ reacts with NH₃, 1° and 2° amines and form an ionic compound.

However, with 3° amine, B_2H_6 forms an adduct. $B_2H_6 + 2N(CH_3)_3 \longrightarrow 2(CH_3)_3N \rightarrow BH_3$

14. (c):
$$R_1 = H$$
 and $R_2 = R_3 = CH_3$

$$R_1$$
 $N-R_3 = H$ $N-CH_3$

Secondary amine reacts with nitrous acid to form nitroso amine (yellow liquid).

15.
$$(c, d) : H - C \bigcirc_{O^{-}} \longleftrightarrow H - C \bigcirc_{O^{-}}$$

B.O.
$$=\frac{2+1}{2}=1.5$$

$$\begin{bmatrix} O \\ C \\ O \end{bmatrix}^{2-} \longleftrightarrow \begin{bmatrix} O \\ C \\ O \end{bmatrix}^{2-} \longleftrightarrow \begin{bmatrix} O \\ C \\ O \end{bmatrix}^{2-}$$

B.O. =
$$\frac{2+1+1}{3} = \frac{4}{3} = 1.33$$

C—O bond length in HCOO $^-$ is less than C—O bond length in CO $_3^{2-}$.

16. (a, b, c, d): Isochoric curves,

$$P(V-b) = RT$$

$$P = \frac{R}{(V-b)} \cdot T$$
 : slope = $\frac{R}{V-b}$

Isobaric curves,

$$PV - Pb = RT$$

$$V = \frac{RT}{P} + b$$
 : slope = $\frac{R}{P}$ and intercept = b

Compressibility factor,

$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}; Z > 1$$

i.e., repulsive forces predominate.

17. (a): $\Delta_r H^{\circ} = \Sigma \Delta_f H^{\circ}_{\text{products}} - \Sigma \Delta_f H^{\circ}_{\text{reactants}}$

$$= \left[-1575.0 \text{ kJ mol}^{-1} - \frac{3}{2} \times 241.8 \text{ kJ mol}^{-1} \right]$$
$$- \left[-2021.0 \text{ kJ mol}^{-1} \right]$$

-[-2021.0 k]

 $= +83.3 \text{ kJ mol}^{-1}$

For 1 kg of $CaSO_4 \cdot 2H_2O$

no. of moles
$$=\frac{1000}{172} = 5.81$$

:. Heat change for 5.81 mol of CaSO₄·2H₂O

$$= 5.81 \text{ mol} \times 83.3 \text{ kJ mol}^{-1}$$

= 484 kJ

18. (b): $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

Now, $\Delta S^{\circ} = \Sigma S^{\circ}_{products} - \Sigma S^{\circ}_{reactants}$

$$\Rightarrow \Delta S^{\circ} = \left[130 + \left(\frac{3}{2} \times 188\right)\right] - 194$$
$$= 218 \text{ J K}^{-1} \text{ mol}^{-1} = 0.218 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^{\circ} = 83.3 - (0.218 \times 298)$$
$$= 18.336 \text{ kJ mol}^{-1}$$

 ΔH = +ve and ΔG = +ve hence, reaction is endothermic and non-spontaneous.

- 19. (a, b, c): (a) $1^{\circ}RX$, (b) $1^{\circ}RX$; (c) $\begin{bmatrix} & & & & \\ & -C & & \end{bmatrix}$ group at α C-atom favours S_N^2 reaction. (d) Neopentyl halide does not undergo either S_N^2 and S_N^2 .
- **20.** (c): Neighbouring group participation of COOgroup, with retention of configuration takes place.

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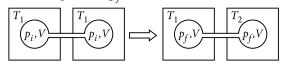
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We are happy to inform our readers that most of the questions asked in JEE Main 2016 Exam are very similar to the problems given in MTG JEE Main Chemistry.



- 1. At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20% O2 by volume for complete combustion. After combustion the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is
 - (a) C_3H_6
- (b) C_3H_8
- (c) C_4H_8
- (d) C_4H_{10}
- Two closed bulbs of equal volume (V) containing an ideal gas initially at pressure p_i and temperature T_1 are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to T_2 . The final pressure p_f is



- (c) $2p_i \left(\frac{T_2}{T_1 + T_2}\right)$ (d) $2p_i \left(\frac{T_1 T_2}{T_1 + T_2}\right)$
- 3. A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference V esu. If e and m are charge and mass of an electron respectively, then the value of h/λ (where λ is wavelength associated with electron wave) is given by

- (a) meV
- (b) 2meV
- (c) \sqrt{meV}
- (d) $\sqrt{2meV}$
- **4.** The species in which the N atom is in a state of sp hybridisation is
 - (a) NO_2^+
- (b) NO_2^-
- (c) NO_3
- (d) NO_2
- The heats of combustion of carbon and carbon monoxide are -393.5 and -283.5 kJ mol⁻¹ respectively. The heat of formation (in kJ) of carbon monoxide per mole is
 - (a) 110.5
- (b) 676.5
- (c) -676.5
- (d) -110.5

[From MTG JEE Main Chemistry, Similar Question, Page 177, Q-60]

- 6. 18 g glucose ($C_6H_{12}O_6$) is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is
 - (a) 7.6
- (b) 76.0
- (c) 752.4
- (d) 759.0

[From MTG JEE Main Chemistry, Page 327, Q-16]

- The equilibrium constant at 298 K for a reaction, $A + B \rightleftharpoons C + D$ is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L^{-1}) will be
 - (a) 0.182
- (b) 0.818
- (c) 1.818
- (d) 1.182

[From MTG JEE Main Chemistry, Similar Question, Page 206, Illustration-6]

- 8. Galvanization is applying a coating of
 - (b) Cr
- (c) Cu
- (d) Zn

[From MTG JEE Main Chemistry, Similar Question, Page 383, Q-17]

- 9. Decomposition of H₂O₂ follows a first order reaction. In fifty minutes the concentration of H₂O₂ decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H₂O₂ reaches 0.05 M, the rate of formation of O2 will be

 - (a) $6.93 \times 10^{-2} \text{ mol min}^{-1}$ (b) $6.93 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$
 - (c) 2.66 L min⁻¹ at STP
 - (d) $1.34 \times 10^{-2} \text{ mol min}^{-1}$

[From MTG JEE Main Chemistry, Similar Question, Page 416, Q-3]

- 10. For a linear plot of $\log (x/m)$ versus $\log p$ in a Freundlich adsorption isotherm, which of the following statements is correct? (k and n are constants)
 - (a) Both k and 1/n appear in the slope term.
 - (b) 1/n appears as the intercept.
 - (c) Only 1/n appears as the slope.
 - (d) $\log (1/n)$ appears as the intercept.

[From MTG JEE Main Chemistry, Similar Question, Page 438, Q-23]

- 11. Which of the following atoms has the highest first ionization energy?
 - (a) Rb
- (b) Na
- (c) K
- (d) Sc
- 12. Which one of the following ores is best concentrated by froth floatation method?
 - (a) Magnetite
- (b) Siderite
- (c) Galena
- (d) Malachite

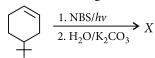
[From MTG JEE Main Chemistry, Similar Question, Page 498, Q-11]

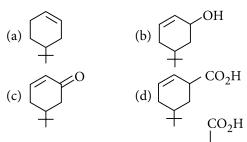
- 13. Which one of the following statements about water is false?
 - (a) Water is oxidized to oxygen during photosynthesis.
 - (b) Water can act both as an acid and as a base.
 - (c) There is extensive intramolecular hydrogen bonding in the condensed phase.
 - (d) Ice formed by heavy water sinks in normal water.
- 14. The main oxides formed on combustion of Li, Na and K in excess of air are, respectively
 - (a) Li₂O, Na₂O and KO₂
 - (b) LiO₂, Na₂O₂ and K₂O
 - (c) Li₂O₂, Na₂O₂ and KO₂
 - (d) Li₂O, Na₂O₂ and KO₂

- 15. The reaction of zinc with dilute and concentrated nitric acid, respectively produces
 - (a) N_2O and NO_2
- (b) NO₂ and NO
- (c) NO and N₂O
- (d) NO₂ and N₂O
- 16. The pair in which phosphorus atoms have a formal oxidation state of +3 is
 - (a) orthophosphorous and pyrophosphorous acids
 - (b) pyrophosphorous and hypophosphoric acids
 - (c) orthophosphorous and hypophosphoric acids
 - (d) pyrophosphorous and pyrophosphoric acids.
- 17. Which of the following compounds is metallic and ferromagnetic?
 - (a) TiO_2
- (b) CrO_2
- (c) VO_2
- (d) MnO₂
- **18.** The pair having the same magnetic moment is [At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27]
 - (a) $[Cr(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$
 - (b) $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$
 - (c) $[Mn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{2+}$
 - (d) $[CoCl_4]^{2-}$ and $[Fe(H_2O)_6]^{2+}$
- 19. Which one of the following complexes shows optical isomerism?
 - (a) $[Co(NH_3)_3Cl_3]$
 - (b) $cis[Co(en)_2Cl_2]Cl$
 - (c) $trans[Co(en)_2Cl_2]Cl$
 - (d) $[Co(NH_3)_4Cl_2]Cl$ (en = ethylenediamine)
- 20. The concentration of fluoride, lead, nitrate and iron in a water sample from an underground lake was found to be 1000 ppb, 40 ppb, 100 ppm and 0.2 ppm, respectively. This water is unsuitable for drinking due to high concentration of
 - (a) fluoride
- (b) lead
- (c) nitrate
- (d) iron.

[From MTG JEE Main Chemistry, Similar Question, Page 774, Q-20]

- 21. The distillation technique most suited for separating glycerol from spent-lye in the soap industry is
 - (a) simple distillation
 - (b) fractional distillation
 - (c) steam distillation
 - (d) distillation under reduced pressure.
- **22.** The product of the reaction given below is





- 23. The absolute configuration of $\begin{array}{c} H - \\ H - \end{array}$ CH₃
 - (a) (2R, 3S)
- (b) (2S, 3R)
- (c) (2S, 3S)
- (d) (2R, 3R)
- [From MTG JEE Main Chemistry, Similar Question, Page 880, Q-78]
- **24.** 2-Chloro-2-methylpentane on reaction with sodium methoxide in methanol yields

(I)
$$C_2H_5CH_2C - OCH_3$$

 CH_3
(II) $C_2H_5CH_2C = CH_2$
 CH_3

(II)
$$C_2H_5CH_2C = CH_2$$

 CH_3

(III)
$$C_2H_5CH = C - CH_3$$

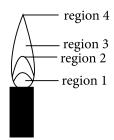
 CH_3

- (a) all of these
- (b) I and III
- (c) III only
- (d) I and II
- **25.** The reaction of propene with HOCl ($Cl_2 + H_2O$) proceeds through the intermediate:
 - (a) $CH_3 CH^+ CH_2 OH$
 - (b) $CH_3-CH^+-CH_2-Cl$
 - (c) $CH_3-CH(OH)-CH_2^+$
 - (d) $CH_3 CHCl CH_2^+$
- 26. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are
 - (a) one mole of NaOH and one mole of Br₂
 - (b) four moles of NaOH and two moles of Br₂
 - (c) two moles of NaOH and two moles of Br₂
 - (d) four moles of NaOH and one mole of Br₂.
- 27. Which of the following statements about low density polythene is false?
 - (a) Its synthesis requires high pressure.
 - (b) It is a poor conductor of electricity.

- (c) Its synthesis requires dioxygen or a peroxide initiator as a catalyst.
- (d) It is used in the manufacture of buckets, dust-bins etc.
- 28. Thiol group is present in
 - (a) cytosine
- (b) cystine
- (c) cysteine
- (d) methionine.
- 29. Which of the following is an anionic detergent?
 - (a) Sodium stearate
 - (b) Sodium lauryl sulphate
 - (c) Cetyltrimethyl ammonium bromide
 - (d) Glyceryl oleate

[From MTG JEE Main Chemistry, Similar Question, Page 1237, Q-24]

30. The hottest region of Bunsen flame shown in the figure below is



- (a) region 1
- (b) region 2
- (c) region 3
- (d) region 4.

SOLUTIONS

1. (b): Chemical equation for the combustion of hydrocarbon is

$$C_x H_{y(g)} + \left(x + \frac{y}{4}\right) O_{2(g)} \longrightarrow x CO_{2(g)} + \frac{y}{2} H_2 O_{(l)}$$

$$15\left(x+\frac{y}{4}\right)$$
mL

Initial 15 mL $15\left(x+\frac{y}{4}\right)$ mL 0 Final 0 0 15x mL Now, volume of O₂ in air = $\frac{20}{100}$ × 375 = 75 mL

$$\therefore 75 = 15\left(x + \frac{y}{4}\right) \implies x + \frac{y}{4} = 5$$

Out of given four options, C₃H₈ will satisfy the above equation.

2. (c): Initially, number of moles of gas in each bulb is

$$n_1 = \frac{p_i V}{RT_1}$$
 and $n_2 = \frac{p_i V}{RT_1}$

After the temperature of second bulb is raised to T_2 then the number of moles of gas in both the bulbs are

$$n'_1 = \frac{p_f V}{RT_1}$$
 and $n'_2 = \frac{p_f V}{RT_2}$

Now, the total number of moles of gas in both the bulbs remains same in both the cases.

$$\begin{split} n_1 + n_2 &= n_1' + n_2' \\ \frac{2p_i V}{RT_1} &= \frac{p_f V}{RT_1} + \frac{p_f V}{RT_2} \\ \frac{2p_i V}{RT_1} &= \frac{p_f V}{R} \left(\frac{T_2 + T_1}{T_1 T_2}\right) \\ p_f &= \frac{2p_i T_2}{T_1 + T_2} \end{split}$$

3. (d):
$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mK.E.}} = \frac{h}{\sqrt{2meV}}$$
 (: K.E. = eV]
$$\frac{h}{\lambda} = \sqrt{2meV}$$

4. (a):
$$[O = N = O]^+$$

sp hybridisation





5. (d): The required equation is

$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}; \Delta H_f = ?$$

Given that

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}; \Delta H_1 = -393.5 \text{ kJ/mol}^{-1}$$
...(i)

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}; \Delta H_2 = -283.5 \text{ kJ mol}^{-1}$$
...(ii)

Subtracting eqn (ii) from eqn (i) will give the required equation.

$$\Rightarrow \Delta H_f = \Delta H_1 - \Delta H_2 = -393.5 - (-283.5)$$

= -110 kJ mol⁻¹

6. (c): Number of moles of glucose $(n_{C_6H_{12}O_6})$

$$=\frac{18}{180}=0.1 \text{ mol}$$

Number of moles of water $(n_{\text{H}_2\text{O}}) = \frac{178.2}{18} = 9.9 \text{ mol}$

Mole fraction of water in solution (x_{H_2O})

$$= \frac{n_{\text{H}_2\text{O}}}{n_{\text{H}_2\text{O}} + n_{\text{C}_6\text{H}_12\text{O}_6}} = \frac{9.9}{10} = 0.99$$

Vapour pressure of water in aqueous solution,

$$p_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}}^{\circ} x_{\text{H}_2\text{O}} = 760 \text{ torr} \times 0.99 = 752.4 \text{ torr}$$

7. (c): $A + B \rightleftharpoons C + D$ Initial conc. $1 \quad 1 \quad 1 \quad 1 \quad 1$ At equilibrium $1-x \quad 1-x \quad 1+x \quad 1+x$

Now,
$$K_c = \frac{[C][D]}{[A][B]}$$

i.e.,
$$100 = \frac{(1+x)^2}{(1-x)^2} \implies 10 = \frac{1+x}{1-x}$$

 $10 - 10x = 1 + x \implies 9 = 11x \implies x = 0.818$

So, concentration of D at equilibrium = 1 + 0.818 = 1.818 M

 (d): Galvanization is a method of rust prevention by applying zinc coating which acts as a sacrificial metal.

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9. (b): Decomposition of H_2O_2 is represented as $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$

Concentration of $\rm H_2O_2$ decreases from 0.5 M to 0.125 M in 50 minutes *i.e.*, reduced to $\frac{1}{4}$ th .

So, it can be represented as

$$0.5 \xrightarrow{t_{1/2}} 0.25 \xrightarrow{t_{1/2}} 0.125$$
50 min

 \Rightarrow $2t_{1/2} = 50 \text{ min} \Rightarrow t_{1/2} = 25 \text{ min}$

Now, for a first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{25} \,\mathrm{min}^{-1}$$

Rate of H_2O_2 decomposition = $k[H_2O_2]$

$$= \frac{0.693}{25} \times (0.05) = 1.386 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

Rate of formation of $O_2 = \frac{1}{2} \times \text{rate of } H_2O_2$ decomposition

$$= \frac{1}{2} \times 1.386 \times 10^{-3}$$
$$= 6.93 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$$

10. (c): For the Freundlich adsorption isotherm, equation is

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log p$$

Now, comparing this equation with y = mx + c, slope $(m) = \frac{1}{n}$; intercept $(c) = \log k$

- 11. (d): Rb, Na and K belong to group 1 which on losing one electron attain noble gas configuration and thus, have low value of ionisation energies. On the other hand, Sc with electronic configuration [Ar] $3d^44s^2$ loses its electron from 4s-orbital thus, it does not achieve that much stable configuration as in group 1 elements. Hence, it shows higher first ionisation energy.
- **12. (c)**: Froth floatation method is suitable for sulphide ores thus, PbS *i.e.*, galena is best concentrated by this method.
- 13. (c): In the condensed phase, there is extensive intermolecular hydrogen bonding in water molecules but not intramolecular hydrogen bonding.

- 14. (d): Li + O_2 \longrightarrow Li₂O Normal oxide 2Na + O_2 \longrightarrow Na₂O₂ Peroxide K + O₂ \longrightarrow KO₂ Superoxide
- 15. (a): $4\text{Zn} + 10\text{HNO}_{3(\text{dil.})} \longrightarrow 4\text{Zn}(\text{NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}$ $\text{Zn} + 4\text{HNO}_{3(\text{conc.})} \longrightarrow \text{Zn}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
- 16. (a): NameFormulaOxidation stateOrthophosphorous acid H_3PO_3 +3Pyrophosphorous acid $H_4P_2O_5$ +3Hypophosphoric acid $H_4P_2O_6$ +4Pyrophosphoric acid $H_4P_2O_7$ +5
- 17. (b): CrO₂ is metallic and ferromagnetic.
- 18. (b): $[Cr(H_2O)_6]^{2+}$ $Cr^{2+} \rightarrow [Ar]3d^44s^0$ $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \downarrow$ 4 unpaired electrons

| CoCl₄|²⁻ | Co²⁺
$$\rightarrow$$
 [Ar]3 d^74s^0 | ds | ds

$$\begin{aligned} \left[\text{Fe(H}_2\text{O)}_6 \right]^{2+} \\ \text{Fe}^{2+} &\to \left[\text{Ar} \right] 3d^6 4s^0 \\ &\xrightarrow{3d} & 4s \\ &\downarrow \downarrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \\ &\text{4 unpaired electrons} \end{aligned}$$

[Mn(H₂O)₆]²⁺
Mn²⁺
$$\rightarrow$$
 [Ar]3 d^54s^0

$$3d \qquad 4s$$

$$5 \text{ unpaired electrons}$$

Hence, $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ have same number of unpaired electrons *i.e.*, same magnetic moment.

19. (b): [Co(NH₃)₃Cl₃] has two geometrical isomers but both are optically inactive due to plane of symmetry.

cis[Co(en)2Cl2]Cl is optically active.

$$en$$
 Cl Cl en co en co co en co en

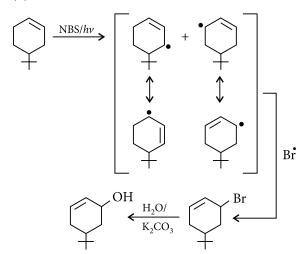
Non-superimposable

trans[Co(en)2Cl2]Cl is optically inactive due to plane of symmetry.

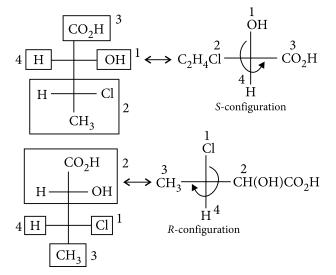
[Co(NH₃)₄Cl₂]Cl has two geometrical isomers but both are optically inactive due to plane of symmetry.

- 20. (c): Fluoride, lead and iron are present within their permissible limits but nitrate ion which has permissible value of 50 ppm, is present in much higher amount i.e., 100 ppm which makes the water unfit for drinking.
- 21. (d): Glycerol is separated from spent-lye by distillation under reduced pressure because under normal distillation glycerol having boiling point of 290°C may decompose.

22. (b):



23. (b):



24. (a): The reaction can follow $S_N \mathbf{1}$ or E_2 mechanism thus, all the given three products are possible.

or
$$CH_3$$

$$C_2H_5CH_2-C=CH_2$$

25. (b): $HOCl \longrightarrow OH + Cl^+$

$$CH_{3}-CH \stackrel{\frown}{=} CH_{2} \stackrel{Cl^{+}}{\longrightarrow} CH_{3}-\stackrel{+}{C}H-CH_{2}-Cl$$

$$\xrightarrow{OH^{-}} CH_{3}-CH-CH_{2}-Cl$$

$$OH$$

$$OH$$

$$OH$$

$$26. (d): R-C-NH_{2}+Br_{2}+4NaOH \longrightarrow$$

26. (d):
$$R - \overset{\text{ii}}{C} - \text{NH}_2 + \text{Br}_2 + 4\text{NaOH} \longrightarrow R\text{NH}_2 + 2\text{NaBr} + \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}$$

27. (d): High density polythene is used to manufacture buckets, dust-bins, etc. while low density polythene is used for manufacturing flexible pipes, insulation of electrical wires etc. due to its poor conductivity and slight flexibility.

28. (c): Cysteine:
$$HS - CH_2 - CH$$

Thiol group

COOH

- 29. (b): Sodium lauryl sulphate: CH₃(CH₂)₁₁OSO₃ Na⁺
- **30. (b)**: Region-2 is the blue flame which is the hottest region of Bunsen flame.

OPINION POLL

Do you agree with the govt's decision to not give weightage to Class XII board marks in JEE (Main)?





CONCEPT BOOSTER



Hello students!! Hope you all are doing fine. Chemistry is a subject of Concepts as you can see both of them starts with 'C' . This month, I am presenting Concepts of Acids and Bases and this is the first phase. You have seen that questions on Acids and Bases have always been an important topic in JEE. Hope you will like and appreciate my efforts as before.

*Arunava Sarkar

IMPACT OF ELECTRONIC EFFECTS ON ACIDITY AND BASICITY

Acidity Corner

○ Concept-1: Electron withdrawing groups (EWGs) i.e., -I and -R effect containing groups increase acidity whereas electron donating groups (EDGs) decrease acidity. EDGs are those groups which contain +I and +R effects.

	Compound	pK _a
Ī	CH ₃ COOH	4.8
ľ	FCH ₂ COOH	2.7
ľ	ClCH ₂ COOH	2.8
ľ	BrCH ₂ COOH	2.9
İ	ICH ₂ COOH	3.1

So, according to the acidic strength the order is : FCH₂COOH > ClCH₂COOH > BrCH₂COOH > ICH₂COOH > CH₃COOH

○ Concept-2: More will be the number of –*I* effect containing groups, more will be the acidity. For example,

Compound	pK _a
CCl₃COOH	0.64
ClCH₂COOH	2.8
Cl₂CHCOOH	1.3

So, as per the acidity the order is:

CCl₃COOH > Cl₂CHCOOH > ClCH₂COOH

• Concept-3: Formic acid is stronger than benzoic

Compound	pK_a
НСООН	3.8
C ₆ H₅COOH	4.2

Both the compounds have stabilized corresponding carboxylates and therefore, they can release H⁺.

$$\begin{array}{c} O \\ H-C-O-H \longrightarrow \begin{bmatrix} & & & \\$$

Now, in case of
$$\bigoplus_{\mathbf{Z}} \overset{O}{=} \ddot{\ddot{O}}$$

This H does not do anything.

Resonance hybrid

^{*} Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

But, in case of
$$C - \ddot{O}$$

This Ph-group has both -I and +R effects.

-I is electron withdrawing whereas +R is electron donating. Point to be noted is +R > -I. Hence, overall,

benzoate
$$\begin{pmatrix} O \\ | C - \vec{O} \end{pmatrix}$$
 ion is destabilised and its

stability is lesser than that of HCO \ddot{O} . This is why as per acidity, HCOOH > PhCOOH.

Oconcept-4: CF_3COOH is 10^5 times stronger than CH_3COOH . CF_3COOH is having a pK_a value of 0.2 (in some books it is given as zero which is probably not correct). There are so many acids with the negative values of pK_a as shown below:

Compound	pK_a
HI	-10
HBr	-9
HCl	-7
H_2SO_4	-5
HNO ₃	-1.3
	0.0
$CH_3 - C \equiv \stackrel{+}{N}H$	-10.1
$CH_3 - \dot{S}H_2$	-6.8
СН ₃ СН ₂ О́ −Н Н	-2.4
CH ₃ SO ₃ H	-1.2

○ Concept-5: Two chlorine atoms have more electron withdrawing power than that of single fluorine (-F) atom. *i.e.*, Cl₂CHCOOH is more powerful acid than FCH₂COOH.

Compound	p <i>K</i>	а
Cl₂CHCOOH	1.3	double
FCH₂COOH	2.6	double

 Concept-6: Among the weak inorganic acids (mostly those which is often used), the following acidity order is observed.

$$H_2CO_3 > H_2S > HCN$$

Compound	pK_a
H_2CO_3	6.4
H_2S	7.0
HCN	9.1

Oconcept-7: For alcohols, if R is bigger, pK_a will be more and more. So, as per acidity the following order between thiol, methanol, water and higher alcohol is observed.

Thiol (RSH) > $CH_3OH > H_2O > CH_3CH_2OH$

Compound	pK_a
CH ₃ CH ₂ SH	10.5
CH ₃ OH	15.5
H_2O	15.7
CH ₃ CH ₂ OH Bigger alkyl(+R) group	16.0

 Concept-8: Acidic character of the compounds (aliphatic or aromatic) containing carbonyl group (⊂ = O) is given in the following table.

Compound	pK_a
Organic acid (aliphatic) O CH ₃ - C-OH	4.8
О СН ₃ —С—Н	17
CH_3-C-CH_3	20
CH ₃ -C-OEt	24.5
$CH_3 - C - NH_2$	16
O CH ₃ -C-O-O-H (Peracid)	8.2
$\bigcirc -\stackrel{\mathrm{O}}{\vdash} -\mathrm{CH}_{3}$	16.0
О Н-С-ОН	3.8
CH_3 C CH_2 C	10.7

$\begin{array}{ccc} & & & O \\ & & & & \\ CH_3-C-CH_2-C-CH_3 \end{array}$	8.9
НСНО	13.3
Organic acid (aromatic) C ₆ H ₅ COOH	4.2
C ₆ H ₅ CHO	14.9

The general acidity order of the compounds containing C=O group is:

Organic acid > peracid > aliphatic diketone > β -keto ester > HCHO > benzaldehyde (PhCHO) > acid amide > aliphatic aldehyde (other than HCHO) > aliphatic ketone > aromatic ketone > acid halide (-F > -Cl > -Br > -I) > acid anhydride > ester (In many occassions, exception to the above order is observed because for specific class or specific compound slight changes may appear).

- Concept-9: Acidity of hydrocarbons is always a great area of interest. Their acidity order is: alkyne > alkene > alkane (decreasing order of acidity)
 - But when popular hydrocarbons intervene then the acidity can be written on the basis of pK_a values as given below:

given below.	
Compound	pK_a
CH ₄	50
CH ₃ —CH ₃	50
CH ₂ =CH ₂	44
CH ₂ =CH-CH ₃	43
	43
	41
	46
$\begin{bmatrix} \mathrm{NH_3} \\ \mathrm{CH_3}\mathrm{NH_2} \\ \mathrm{H_2} \end{bmatrix}$	36 40 40 study with 35 hydrocarbons
НС≡СН	25

Hence, the acidity order is:

-C≡C-> H_2 > NH_3 > CH_3NH_2 (other aliphatic amines) > toluene (for other alkyl substituted benzene it may differ) > benzene \approx CH_3CH = CH_2

>
$$CH_2 = CH_2$$
 > alkanes ($CH_4 \approx CH_3 - CH_3$)
$$sp^3$$

- Oconcept-10: In case of inorganic acids there are a few points which should be remembered.
 - (a) For oxy acids, with the increase in the oxidation number of the central element acidic nature increases. For example,

$$^{+7}_{\text{HClO}_4} > \text{H}_2^{+6}_{\text{SO}_4} > \text{H}_2^{+4}_{\text{SO}_3} > \text{HNO}_2$$

(b) The above rule is also valid for the same central element or key element. For example,

$$^{+7}_{\text{HClO}_4} > \text{HClO}_3 > \text{HClO}_2 > \text{HOCl (HClO)}$$

(c) For moving from left to right in the same period acidity increases.

$$H_2SiO_4 < H_3PO_4 < H_2SO_4 < HClO_4$$

(d) If electronegativity increases, acidic nature also increases. For example,

$$HClO_4 > HBrO_4 > HIO_4$$

(e) If you keep oxidation state same then bigger atom containing acid will be less acidic.

(f) If more electronegative atom is attached with H atom then this will create higher acidity in the compound. For example,

$$H-F > H-OH > H-NH2 > H-CH3$$

(g) If the orbital overlapped with the 1s-orbital of H is bigger then the overlapping becomes weak and release of proton becomes easy. This is why, acidic order is HI > HBr > HCl > HF.

or
$$H_2Te > H_2Se > H_2S > H_2O$$

The glimpse of acidic character of inorganic acids is represented in the following table.

Compound	pK_a
HI	-10
HBr	-9
HCl	-7
H ₂ SO ₄	-5
$ m H_2SO_4 \ H_3O^+$	-1.7
HNO_3	-1.3
HF	3.2
HNO_2	3.4

H ₃ PO ₄	2.1
H ₂ CO ₃	6.4
H ₂ S	7.0
HCN	9.2
H ₂ O	15.7
Just for CH ₃ O	H 15.5
comparative C ₂ H ₅ (
study PhOH	10.0
Just for comparative NH ₃	NH ₃ 8.1 36
study CH ₃ NF	I_2 40
LH ₂	35
HCO ₃	10.2
$H_2PO_4^-$	7.2
HSO ₄	2.0
Just for CH ₃ CO comparative study NH ₄ ⁺	OH 4.75 or 4.8 9.2

Hence, the acidity order is:

$$\begin{split} & \text{HClO}_4 > \text{HI} > \text{HBr} > \text{HCl} > \text{H}_2 \text{SO}_4 > \text{H}_3 \text{O}^+ > \text{HNO}_3 \\ & > \text{HSO}_4^- > \text{H}_3 \text{PO}_4 > \text{HF} > \text{CH}_3 \text{COOH} > \text{H}_2 \text{CO}_3 \\ & > \text{H}_2 \text{S} > \text{H}_2 \text{PO}_4^- > \text{H}_2 \text{N} - \overset{+}{\text{NH}}_3 > \text{HCN} \approx \text{NH}_4^+ > \\ & \text{PhOH} > \text{CH}_3 \text{OH} > \text{H}_2 \text{O} > \text{C}_2 \text{H}_5 \text{OH} > \text{H}_2 > \text{NH}_3 > \\ & \text{CH}_3 \text{NH}_2 > \text{CH}_4 \approx \text{CH}_3 - \text{CH}_3 \end{split}$$

Therefore, the basic strength of corresponding conjugate base will be

 $CIO_{4}^{-} < I^{-} < Br^{-} < CI^{-} < HSO_{4}^{-} < H_{2}O < NO_{3}^{-} < SO_{4}^{2-} < H_{2}PO_{4}^{-} < F^{-} < CH_{3}COO^{-} < HCO_{3}^{-} < HS^{-} < HPO_{4}^{2-} < NH_{2} - NH_{2} < \bar{C}N \approx NH_{3} < PhO^{-}$

< CH₃O $^-$ < OH < C₂H₅O $^-$ < H $^-$ < NH₂ < CH₃NH < CH₃- CH₂

Oconcept-11:

Compound	pK_a		
Benzene sulphonic acid	2.554		
Benzoic acid	4.2		

So, sulphonic acids are stronger than carboxylic acids.

$$\begin{array}{c} O \\ Ph - S - O - H \xrightarrow{H_2O} Ph - S - O + H_3O^+ \\ O \\ O \\ Benzene \\ sulphonate ion \end{array}$$

Because sulphonate ion is very well resonance stabilized as dispersal of negative charge takes place over three oxygen atoms as shown below:

$$Ph - S \neq \bar{O} \longleftrightarrow Ph - S = O \longleftrightarrow Ph - S = O$$

$$Three equivalent structures$$

$$Fh - S = O \longleftrightarrow Ph - S = O$$

$$Fh - S = O \longleftrightarrow Ph - S = O$$

$$Fh - S = O \longleftrightarrow Ph - S = O$$

$$Fh - S = O \longleftrightarrow Ph - S = O$$

On the other hand,

$$\begin{array}{c}
O \\
| | \\
Ph-C-O-H \xrightarrow{H_2O} Ph-C-O^- + H_3O^+ \\
Benzoic acid Benzoate ion
\end{array}$$

The negative charge over oxygen atom can be dispersed in between two oxygen atoms as shown below:

$$Ph - C \xrightarrow{O} O \xrightarrow{O} Ph - C = O = \begin{bmatrix} O \\ I : \\ Ph - C : O \end{bmatrix}$$
Two equivalent structures \otimes

So, due to more stability of the corresponding conjugate base, benzene sulphonic acid is stronger than benzoic acid. Moreover, due to presence of three highly electronegative oxygen atoms in benzene sulphonic acid, release of H⁺ gets facilitated.

Concept-12: Branching leads to lowering of acidity.
 Consider the following table.

Compound	pK_a
CH ₃ OH	15.5
CH ₃ CH ₂ OH	15.9 or 16.0
CH ₃ CH ₂ CH ₂ CH ₂ OH	16.1
(CH ₃) ₃ COH	17

The reason behind this is that if conjugate base will be highly hindered then it cannot be well solvated so solvation energy will be less and it will lead to the destabilisation of the corresponding conjugate base and lowering of acidity of the corresponding acid.



*Dr. Sangeeta Khanna

1. Which of the following molecules will give maximum rate of reaction with S_N2 mechanism?

(a)
$$CH_3-CH_2-Cl$$
 (b) CH_3-C-CH_2-Cl CH_3 CH_3 CH_3 (c) CH_2-CH_2-Cl (d) $CH_2=CH-Cl$

- 2. Which of the following compounds is maximum reactive towards nucleophile?

(a)
$$CH_3$$
— C — CHO (b) CI — C — CHO

$$CH_3$$

$$CI$$

$$CI$$

3. Which of the following is major product in given reaction?

4. Which of the following is major product in given

(a)
$$(b)$$
 CH_3 CH_3 (c) (d) CH_3 CH_2

Consider the following reaction,

$$CH_{3}-CH-CH_{3} \xrightarrow{(i) CaOCl_{2} + H_{2}O} A + B$$

If product A is CHCl₃ then product B will be

(a)
$$CH_3 - C - OH$$
 (b) $CH_3 - C - CH_3$

O O

(c) $CH_3 - C - C - CH_3$

O O

(d) $CH_3 - C - C - C - CH_3$

- **6.** *p*-type semiconductor is formed when
 - (i) As impurity is mixed in Si
 - (ii) Al impurity is mixed in Si
 - (iii) B impurity is mixed in Ge
 - (iv) P impurity is mixed in Ge
 - (a) (i) and (ii)
- (b) (i) and (iv)
- (c) (ii) and (iii)
- (d) (ii) and (iv)
- Plot of $\log x/m$ against $\log P$ is a straight line inclined at an angle of 45°. When the pressure is 0.5 at m and Freundlich parameter, k is 10, the amount of solute adsorbed per gram of adsorbent will be $(\log 5 = 0.6990)$
 - (a) 1 g (b) 2 g
- (c) 3 g
- (d) 5 g
- 8. Paramagnetic oxides are
 - (a) N_2O_4 , NO_2
- (b) NO, ClO₂
- (c) P_4O_6 , P_4O_{10}
- (d) N_2O_5 , O_2^+

- **9.** The rate law for a reaction between the substances A and B is given by rate = $k[A]^n[B]^m$. On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as
 - (a) $1/2^{m+n}$
- (b) (m + n)
- (c) (n m)
- (d) $2^{(n-m)}$
- **10.** Which of the following can exhibit geometrical isomerism?
 - (a) $[MnBr_4]^{2-}$
- (b) $[Pt(NH_3)_3Cl]^+$
- (c) $[PtCl_2(PPh_3)_2]$
- (d) $[Fe(H_2O)_5NO]^{2+}$
- 11. Xenon oxytetrafluoride is
 - (a) square planar
- (b) square bipyramidal
- (c) octahedral
- (d) square pyramidal.
- 12. Consider a binary mixture of volatile liquids. If at $x_A = 0.4$ the vapour pressure of solution is 580 torr then the mixture could be

$$(p_A^{\circ} = 300 \text{ torr}, p_B^{\circ} = 800 \text{ torr})$$

- (a) $CHCl_3 CH_3COCH_3$ (b) $C_6H_5Cl C_6H_5Br$
- (c) $C_6H_6 C_6H_5CH_3$
- (d) $nC_6H_{14} nC_7H_{16}$
- 13. Solution having osmotic pressure nearer to that of an equimolar solution of $K_4[Fe(CN)_6]$ is
 - (a) Na_2SO_4
- (b) BaCl₂
- (c) $Al_2(SO_4)_3$
- (d) $C_{12}H_{22}O_{11}$
- **14.** 4*f* ¹⁴ configuration is observed in
 - (a) Dy and Pm
- (b) Lu and La
- (c) Yb and Lu
- (d) Tm and Lu.
- **15.** Given that (at T = 298 K)

 $Cu_{(s)}|Cu^{2+}(1.0 \text{ M})||Ag^{+}(1.0 \text{ M})|Ag_{(s)}; \quad E_{cell}^{\circ} = 0.46 \text{ V}$ $Zn_{(s)}|Zn^{2+}(0.1 \text{ M})||Cu^{2+}(1.0 \text{ M})|Cu_{(s)}; \quad E_{cell}^{\circ} = 1.10 \text{ V}$ Then E_{cell} for

 $Zn|Zn^{2+}(0.1 \text{ M})||Ag^{+}(1.0 \text{ M})|Ag \text{ at } 298 \text{ K will be}$

- (a) 1.59 V
- (b) 1.53 V
- (c) 2.53 V
- (d) cannot be calculated due to insufficient data.
- **16.** Which of the following options show correct matches?

Column I

Column II

- (i) Kohlrausch law p. $\frac{\Lambda_n^c}{\Lambda_n^{\circ}}$
- (ii) Molar q. $\frac{1}{R}$
- (iii) Specific r. Λ_m° of $Ca_3(PO_4)_2$ conductance (κ) = $3(\Lambda_m^{\circ})_{Ca^{2+}}$ + $2(\Lambda_m^{\circ})_{PO_3}^{3-}$
- (iv) Degree of ionisation s. $\frac{\kappa \times 1000}{M}$

- (a) (i) r, (ii) p, (iii) q, (iv) s
- (b) (i) s, (ii) p, (iii) q, (iv) s
- (c) (i) r, (ii) s, (iii) q, (iv) p
- (d) (i) p, (ii) s, (iii) q, (iv) r
- **17.** A fuel cell involves combustion of the butane at 1 atm and 298 Kelvin

$$C_4H_{10(g)} + \frac{13}{2}O_{2(g)} \longrightarrow 4CO_{2(g)} + 5H_2O_{(l)};$$

 $\Delta G^{\circ} = -2746 \text{ kJ/mole}$

What is E° of this cell?

- (a) +4.74 V
- (b) +0.547 V
- (c) +1.09 V
- (d) +4.37 V
- **18.** An element "A" has face centered cubic structure with edge length equal to 361 pm. The radius of atom "A" is
 - (a) 127.6 pm
- (b) 180.5 pm
- (c) 160.5 pm
- (d) 64 pm
- **19.** LiF and CsI are less soluble in water. What factors are responsible for this?
 - (a) LiF: High ionic character
 - CsI: High covalent character
 - (b) LiF: Strong reductant
 - CsI : Strong reductant
 - (c) LiF: High Hydration
 - CsI: Less Hydration
 - (d) LiF: High lattice energy
 - CsI: Low hydration energy
- **20.** In the disproportionation reaction :

 ${\rm H_3PO_2} \rightarrow {\rm PH_3} + {\rm H_3PO_3};$ if molecular weight of ${\rm H_3PO_2}$ is m then the equivalent mass of ${\rm H_3PO_2}$ will be

- (a) $\frac{3m}{4}$
- (b) $\frac{4}{3}m$
- (c) $\frac{3m}{5}$
- (d) none of these.
- **21.** Which of the following order is correct?
 - (a) Si Si > C C > Ge Ge (Bond energy)
 - (b) H H > F F > C C (Bond energy)
 - (c) Ge < Sn < Pb (Ability of ns^2e^- to participate in bonding)
 - (d) $SiH_4 > SnH_4 > PbH_4 > CH_4$ (ease of hydrolysis)
- **22.** Match the following:

Element Property

- (i) C p. Used as semiconductor
- (ii) Pb q. Forms most acidic oxide
- (iii) Si r. Commonly found in +2 state
- (iv) Ge s. Purified by zone refining

- (a) (i) s, (ii) r, (iii) q, (iv) p
- (b) (i) p, (ii) q, (iii) r, (iv) s
- (c) (i) q, (ii) s, (iii) p, (iv) r
- (d) (i) q, (ii) r, (iii) p, (iv) s
- 23. The variation of extent of adsorption $\left(\frac{x}{m}\right)$ with pressure at a given constant temperature is given in following figure:



Which of the following relations between temperatures is correct?

- (a) $T_1 = T_2 = T_3$
- (b) $T_1 < T_2 < T_3$
- (c) $T_3 < T_2 < T_1$
- (d) Cannot be predicted
- 24. Oxyacid with maximum P—H bonds is
 - (a) hypophosphorous acid
 - (b) cyclotrimetaphosphoric acid
 - (c) hypophosphoric acid
 - (d) orthophosphorous acid.
- 25. 0.85% w/V solution of NaNO₃ is 90% dissociated at 27°C. Calculate its osmotic pressure (in atm).
 - (a) 4.67 atm
- (b) 5.74 atm
- (c) 3.23 atm
- (d) 46.4 atm
- 26. Ozone can be quantitatively estimated by
 - (a) KI, Na_2SO_4
- (b) PbS, Na₂SO₄
- (c) NO, I₂
- (d) KI, $Na_2S_2O_3$
- 27. Which of the following orders is correct?
 - (a) HF > HCl > HBr > HI (Melting point)
 - (b) $F_2 > Cl_2 > Br_2 > I_2$ (Bond energy)
 - (c) HOCl > HClO₂ > HClO₃ > HClO₄ (oxidising nature)
 - (d) $F_2 > Br_2 > Cl_2 > I_2$ (oxidising nature)
- 28. Which of the following orders is correct?
 - (a) He > Ne > Ar > Kr (Adsorption tendency)
 - (b) He > Ne > Ar > Kr (Critical temperature)
 - (c) He > Ne > Ar > Kr (Boiling point)
 - (d) Xe > Kr > Ar > Ne (Polarisation)
- 29. 99% of a first order reaction was completed in 64 minutes, when will 99.9% of the reaction get completed?
 - (a) 50 min
- (b) 48 min
- (c) 32 min
- (d) 96 min
- **30.** For the reaction,

N_{2(g)} + 3H_{2(g)}
$$\Longrightarrow$$
 2NH_{3(g)}; $K_p = 5 \times 10^{-5}$ at 25°C ΔG° for the reaction will be ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$)

- (a) 24.5 kJ
- (b) 40.5 kJ
- (c) -7.3 kJ
- (d) -40.5 kJ
- 31. $CH_3 C \equiv C H \xrightarrow{2HCl} A \xrightarrow{Zn} B$; B is

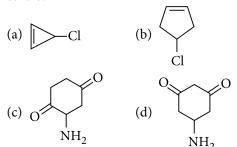
(a)
$$CH_3-C\equiv C-H$$
 (b) $CH_3-C\equiv C-CH_3$
(c) $CH_3-CH=CH_2$ (d) $C=C$

- 32. How many moles of Na⁺ ions are there in 20 mL of $0.4 \text{ M Na}_3\text{PO}_4$?

 - (a) 0.008 (b) 0.024 (c) 0.05
- (d) 0.20
- 33. $H_2NCOCH_2CH_2CONH_2 \xrightarrow{Br_2, OH^-}$
 - (a) H₂NCO(CH₂)₃NH₂
 - (b) BrNHCO(CH₂)₃CONH₂
 - (c) BrNHCO(CH₂)₃CONHBr
 - (d) $H_2N(CH_2)_2NH_2$
- **34.** The IUPAC name of \bigcap is
 - (a) 3, 4-dimethylpentanoyl chloride
 - (b) 1-chloro-1-oxo-2, 3-dimethylpentane
 - (c) 2-ethyl-3-methylbutanoyl chloride
 - (d) 2, 3-dimethylpentanoyl chloride.
- **35.** The products (*A*) and (*B*) of the following reaction, $CH_3CH_2NH_2 + CH_3MgBr \rightarrow A + B$
 - (a) CH₃CH₂CH₃ and NH₂MgBr
 - (b) CH₃CH₂NHCH₃ and MgBr₂
 - (c) CH₃CH₂N(CH₃)₂ and MgBr₂
 - (d) CH₃CH₂NHMgBr and CH₄
- **36.** An example of Perkin's reaction is
 - (a) $C_6H_5CHO + CH_3NO_2 \xrightarrow{KOH}$ $C_6H_5CH=CHNO_2$
 - (b) $C_6H_5CHO + CH_2(COOH)_2$ Alc. NH_3 C₆H₅CH=CHCOOH
 - (c) $C_6H_5CHO + CH_3CHO \xrightarrow{NaOH} C_6H_5CH=CHCHO$
 - (d) $C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa}$ C₆H₅CH=CHCOOH
- 37. Which of the following is known as oil of wintergreen?

 - (a) Phenyl benzoate (b) Phenyl salicylate
 - (c) Phenyl acetate
- (d) Methyl salicylate

38. Which of the following compounds has asymmetric centre?



39. Select the compound in which the lone pair of nitrogen is not delocalised over the benzene ring.

(a)
$$NH - CH_3$$
 (b) NH_2 (c) NH_3F (d) NH_2 OCH₃

40. The final product(s) of this reaction is/are

$$CHCl_3 \longrightarrow X \xrightarrow{50\% \text{ KOH}} X$$

$$OH \qquad OH$$

$$(a) \qquad CH_2 \longrightarrow CH_2OH$$

$$(b) \qquad CH_2OH \longrightarrow COOK$$

$$(c) \qquad OH \qquad COOK$$

$$OH \qquad OH \qquad COOK$$

$$(d) \qquad COOK$$

41. What is *X* in the following reaction? $2CH_3COCH_3 \xrightarrow{Ba(OH)_2} X$

(a)
$$H_3C - C - CH_2 - C - CH_3$$

 CH_3

(b)
$$H_3C - C - CH_2 - CH_2 - CHO$$

 CH_3

(c) CH₃CH(CH₃)CH₂COCH₃

- **42.** Rubber is a polymer of
 - (a) pyrene
- (b) ethylene
- (c) isoprene
- (d) urea.

43.
$$A \xrightarrow{PCl_5} B + H_2 \xrightarrow{Pd-BaSO_4} O$$

(a) $C - H$

(b) NH_2
 $C - NH_2$
 $C - OH$

44. The correct order of ease of dehydration of the following compounds is

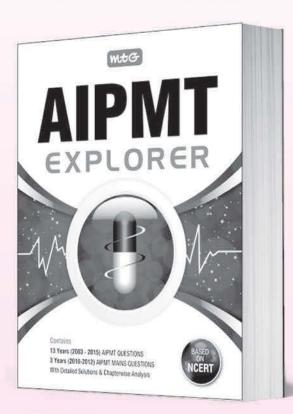
- 45. Which of the following statements is not correct?
 - (a) $K[PtCl_3(\pi-C_2H_4)]$ Zeise's salt has a planar anion.
 - (b) $[Co(NH_3)_3Cl_3]$ will not have optical isomers.
 - (c) In optically active octahedral complex, [Fe(EDTA)]²⁻ coordination number of Fe is six.
 - (d) [Co(NH₃)₅NO₂]Cl and PtCl₂.4NH₃ can be differentiated by AgNO₃ solution qualitatively.

ANSWER KEYS

1.	(c)	2.	(b)	3.	(c)	4.	(b)	5.	(b)
6.	(c)	7.	(d)	8.	(b)	9.	(d)	10.	(c)
11.	(d)	12	(a)	13.	(c)	14.	(c)	15.	(a)
16.	(c)	17.	(c)	18.	(a)	19.	(d)	20.	(a)
21.	(d)	22.	(d)	23.	(c)	24.	(a)	25.	(a)
26.	(d)	27.	(c)	28.	(d)	29.	(d)	30.	(a)
31.	(d)	32.	(b)	33	(d)	34.	(d)	35.	(d)
36.	(d)	37.	(d)	38.	(c)	39.	(c)	40.	(b)
41.	(a)	42.	(c)	43.	(d)	44.	(b)	45.	(d)



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SOLUTIONS

3. (c):
$$Ph$$
 C=O + CH₃CHO OH^- Ph C=CH-CHO + H₂C

5. (b):
$$CH_3 - CH - CH_3 \xrightarrow{CaOCl_2 + H_2O}$$

$$OH \qquad (CH_3COO)_2Ca + CHCl_3$$

$$CH_3COCH_3 + CaCO_3 \xleftarrow{\Delta} \qquad (A)$$

7. **(d)**:
$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$

12. (a):
$$P_{\text{total}} = x_A p_A^{\circ} + x_B p_B^{\circ}$$

= $0.4 \times 300 + 0.6 \times 800 = 600 \text{ torr}$
 $P_{\text{observed}} < P_{\text{total}}$; thus, the deviation is negative.

13. (c):
$$i = 5$$

14. (c): Yb =
$$4f^{14}5d^06s^2$$
; Lu = $4f^{14}5d^16s^2$

$$Cu_{(s)}|Cu^{2+}(1.0 \text{ M})||Ag^{+}(1.0 \text{ M})|Ag_{(s)}; E_{\text{cell}}^{\circ} = 0.46 \text{ V}$$

 $\Delta G^{\circ} = -2F \times 0.46 \quad ...(i)$

For cell,

$$Zn_{(s)}|Zn^{2+}(0.1 \text{ M})||Cu^{2+}(1.0 \text{ M})|Cu_{(s)}; E_{cell}^{\circ} = 1.10 \text{ V}$$

 $\Delta G^{\circ} = -2F \times 1.10$...(ii)

Adding equations (i) and (ii), to get required equation,

$$-2FE_{\text{cell}}^{\circ} = -2F \times 1.10 - 2F \times 0.46$$

 $-E_{\text{cell}}^{\circ} = -1.10 - 0.46$

$$E_{\text{cell}}^{\circ} = 1.56 \text{ V}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^{+}]^{2}}$$

$$E_{\text{cell}} = 1.56 - \frac{0.059}{2} \log 0.1 = 1.56 + 0.03 = 1.59 \text{ V}$$

16. (c)

17. (c):
$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

- 2746 × 10³ = -26 × 96500 × E°_{cell}
 $E^{\circ}_{\text{cell}} = 1.09 \text{ V}$

18. (a):
$$r = \frac{a}{2\sqrt{2}} = \frac{361}{2\sqrt{2}}$$
 pm

21. (d): In option (c), inert pair effect; in option (d), octet expansion is maximum in Si.

25. (a):
$$i = 1 + \alpha = 1 + 0.9 = 1.9$$

Osmotic pressure =
$$i \times \frac{W_B}{M_B} \times \frac{RT}{V}$$

Osmotic pressure =
$$1.9 \times \frac{0.85}{85} \times \frac{0.082 \times 300}{100} \times 1000$$

= 4.67 atm

29. (d):
$$k = \frac{2.303}{64} \log \frac{100}{1}$$

and $k = \frac{2.303}{t} \log \frac{100}{0.1}$; $t = 96 \min$

30. (a):
$$\Delta G^{\circ} = -2.303 \ RT \log K_p$$

31. (d):
$$CH_3$$
 CH_3
 32. (b): No. of moles of Na₃PO₄ =
$$\frac{MV}{1000} = \frac{0.4 \times 20}{1000}$$

No. of moles of Na⁺ =
$$3 \times \frac{0.4 \times 20}{1000} = 0.024$$

33. (d): Hofmann's bromamide reaction

34. (d)

35. (d):
$$CH_3CH_2 - NH + H + CH_3MgBr$$

36. (d) 37. (d)
$$\overline{)}$$
 38. (c)

39. (c):
$$NH_3\bar{F}$$
; no lone pair is present on nitrogen.

43. (d):
$$(A)$$
 COOH PCl_5 COCl Rosenmund reduction Pd-BaSO₄ CHO

44. (b)

45. (d): [Pt(NH₃)₄]Cl₂ and [Co(NH₃)₅NO₂]Cl both will give white ppt. with AgNO₃. [Co(NH₃)₃Cl₃] will have geometrical isomers, *fac* and *mer*.



- 1. A S_N2 reaction at an asymmetric carbon of a compound always gives
 - (a) an enantiomer of the substrate
 - (b) a product with opposite rotation
 - (c) a mixture of diastereomers
 - (d) a single stereoisomer.
- 2. What volume of 2.5 M H_2SO_4 is required to neutralize a solution containing 2.5 g NaOH?
 - (a) 10.2 mL
- (b) 18.4 mL
- (c) 12.5 mL
- (d) 11.89 mL
- 3. 0.1 M H₂SO₄ is diluted to 0.01 M H₂SO₄. Hence, its molar conductance will be
 - (a) 10 times
- (b) $\frac{1}{10}$ times
- (c) 100 times
- (d) 10000 times.
- **4.** In the following sequence of reactions, *B* is

$$CH_3CH_2COOH \xrightarrow{P/Br_2} A \xrightarrow{alc. KOH} B$$

- (a) CH_2 =CH-COOH (b) CH_2 -CH-COOH
- (c) CH₃CH₂COBr
- (d) CH₃CH₂OH
- 5. In NO_3^- ion, number of bond pairs and lone pairs of electrons on nitrogen atom are
 - (a) 2, 2
- (b) 3, 1
- (c) 1, 3
- (d) 4, 0
- **6.** The chemical reaction, $2O_3 \longrightarrow 3O_2$ proceeds as follows:

Step 1 :
$$O_3 \rightleftharpoons O_2 + O$$
(fast)

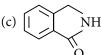
Step 2 : O + O₃
$$\longrightarrow$$
 2O₂(slow)

The rate law expression should be

- (a) $r = k'[O_3]^2$
- (b) $r = k'[O_3]^2[O_2]^{-1}$
- (c) $r = k'[O_3][O_2]$
- (d) unpredictable.

- Which of the following phenols has lowest solubility in water?
 - (a) Phenol
- (b) o-Nitrophenol
- (c) m-Nitrophenol
- (d) p-Nitrophenol
- The complex $[Fe(H_2O)_5NO]^{2+}$ is formed in the brown ring test for nitrates when freshly prepared FeSO₄ solution is added to aqueous solution of NO₃ followed by addition of conc. H₂SO₄. Select the correct statement about this complex.
 - (a) Colour change is due to charge transfer.
 - (b) It has iron in +1 oxidation state and nitrosyl as NO⁺.
 - (c) It has magnetic moment of 3.87 BM confirming three unpaired electrons in Fe.
 - (d) All of these.
- 9. Amount of electricity that can deposit 108 g of silver from AgNO₃ solution is
 - (a) 1 ampere
- (b) 1 coulomb
- (c) 1 faraday
- (d) none of these.
- **10.** The following sequence of reactions on *A* gives

(a)
$$O$$
 (b) O NH



- 11. Which of the following gases is evolved when ammonium dichromate (NH₄)₂Cr₂O₇, is strongly heated?
 - (a) N_2
- (b) N_2O
- (c) NO
- (d) NH₃

- 12. Which of the following is a condensation polymer?
 - (a) Polyisoprene
- (b) Polythene
- (c) Nylon
- (d) Polyacrylonitrile
- **13.** The shape and hybridisation of some xenon oxyfluorides are given. Choose the wrong set.
 - (a) $XeOF_2$ -T-shape- sp^3d
 - (b) XeOF₄-square pyramidal- sp^3d^2
 - (c) XeO₂F₂-distorted trigonal bipyramidal-sp³d
 - (d) XeO_3F_2 -octahedral- sp^3d .
- **14.** Benzene is first treated with conc. HNO₃ and conc. H₂SO₄. Then, the product formed is heated with chlorine and FeCl₃. The final product is
 - (a) 2-chloronitrobenzene
 - (b) 4 -chloronitrobenzene
 - (c) 2,4,6-trichloronitrobenzene
 - (d) 3-chloronitrobenzene.
- **15.** For a reaction $A \rightarrow B$, the rate of reaction quadrupled when the concentration of A is doubled. The rate expression of the reaction is $r = k(A)^n$. The value of n is
 - (a) 1
- (b) 0
- (c) 3
- (d) 2
- **16.** CH₃OC₂H₅ and (CH₃)₃C—OCH₃ are treated with hydroiodic acid. The fragments obtained after reactions are respectively
 - (a) $CH_3I + HOC_2H_5$; $(CH_3)_3C I + HOCH_3$
 - (b) $CH_3OH + C_2H_5I$; $(CH_3)_3CI + HOCH_3$
 - (c) $CH_3OH + C_2H_5I$; $(CH_3)_3C OH + CH_3I$
 - (d) $CH_3I + HOC_2H_5$; $CH_3I + (CH_3)_3C OH$
- 17. The vapour pressure of water at 20°C is 17.54 mm. When 20 g of a non-ionic substance is dissolved in 100 g of water, the vapour pressure is lowered by 0.30 mm. What is the molecular mass of the substance?
 - (a) 200.8 g
- (b) 206.88 g
- (c) 210.5 g
- (d) 215.2 g
- 18. Ferrimagnetism is in
 - (a) $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$
- (b) $\uparrow \downarrow \uparrow \downarrow$
- (c) $\uparrow \uparrow \uparrow \downarrow \downarrow$
- (d) none of these.
- **19.** Methylamine is obtained when acetamide is treated with
 - (a) $Br_2 + NH_4OH$
- (b) NaOH + I_2
- (c) $KOH + Br_2$
- (d) none of these.
- **20.** Helium atom is two times heavier than a hydrogen molecule at 298 K. The average kinetic energy of helium is
 - (a) 2 times of H₂ molecule
 - (b) same as that of H₂ molecule

- (c) 4 times that of hydrogen molecule
- (d) $\frac{1}{2}$ that of H₂ molecule.
- **21.** Which of the following is not a characteristic of physical adsorption?
 - (a) Attraction due to weak van der Waals' forces
 - (b) Irreversible nature of adsorption
 - (c) Multimolecular adsorption layers
 - (d) Decrease in adsorption with increase in temperature.
- **22.** Solubility of sulphates of group 2 elements decreases down the group due to
 - (a) decreasing hydration energy
 - (b) high ionisation energy
 - (c) increase in melting point
 - (d) all of these.

23.
$$CH_3 \xrightarrow{CH_3COCl, Py} X \xrightarrow{KMnO_4} Y$$

The final product 'Y' is a medicine. Which of the following is incorrect regarding 'Y'?

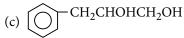
- (a) It has analgesic as well as antipyretic properties.
- (b) It helps to prevent heart attack.
- (c) It has anti-blood clotting action.
- (d) It suppresses the gastric anomalies.
- 24. The number of alcohols that may have the molecular formula 'C₄H₁₀O' but do not have a chiral carbon is
 - (a) 1
- (b) 2
- (c) 3

(c) N

- (d) 4
- **25.** Which of the following has the maximum electronegativity?
 - (a) C
- (b) F
- (d) O
- **26.** When huge amount of sewage is dumped in a river, the BOD will
 - (a) increase
- (b) remain unchanged
- (c) decrease
- (d) may increase or decrease.
- 27. $CH_2CH=CH_2$ on mercuration and demer-

curation produces

(b) CH₂CH₂CH₂OH



(d) none of these.

28. The van der Waals' parameters for gases W, X, Y and Z are

Gas	$a (atm L^2 mol^{-2})$	$b (\mathrm{L} \mathrm{mol}^{-1})$
W	4.0	0.027
X	8.0	0.030
Y	6.0	0.032
Z	12.0	0.027

Which one of these gases has the highest critical temperature?

- (a) W
- (b) X
- (c) Y
- (d) Z
- **29.** Predict the product of reaction of I_2 with H_2O_2 in basic medium.
 - (a) I⁻
- (b) I₂O₃ (d) I₃⁻
- (c) IO_3^-
- 30. What is the free energy change when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure?
 - (a) 540 cal
- (b) -9800 cal
- (c) 9800 cal
- (d) 0 cal
- 31. The average osmotic pressure of human blood is 7.8 bar at 37°C. What is the concentration of an aqueous NaCl solution that could be used in the blood stream?
 - (a) 0.16 mol/L
- (b) 0.31 mol/L
- (c) 0.60 mol/L
- (d) 0.45 mol/L
- 32. Which of the following compounds is thermally least stable?
 - (a) Li₂CO₃
- (b) MgCO₃
- (c) BaCO₃
- (d) BeCO₃
- 33. Which of the following is most stable carbocation?









- **34.** The composition of carnallite is
 - (a) KCl·MgCl₂·6H₂O (b) Na₂Al₂O₃
 - (c) Fe_3O_4
- (d) Na₃AlF₆
- **35.** A tripeptide is written as Glycine-Alanine-Glycine. The correct structure of the tripeptide is

(a)
$$NH_2$$
 O CH_3 NH $COOH$

(b)
$$NH_2$$
 O CH_3 NH $COOH$

(c)
$$NH_2 \cap NH \cap COOH$$
 OCH_3

- **36.** Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being
 - (a) lesser energy difference between 5*f* and 6*d* than between 4f and 5d orbitals
 - (b) more energy difference between 5*f* and 6*d* than between 4f and 5d orbitals
 - (c) more reactive nature of the actinoids than the lanthanoids
 - (d) 4f orbitals are more diffused than the 5f orbitals.
- 37. A compound on analysis was found to contain C = 18.5%, H = 1.55%, Cl = 55.04% and O = 24.81%. Its empirical formula is
 - (a) C₂H₂OCl
- (b) CH₂ClO
- (c) CHClO
- (d) ClCH2O
- 38. H₂S gas when passed through a solution of cations containing HCl precipitates the cations of second group of qualitative analysis but not those belonging to the fourth group. It is because
 - (a) presence of HCl decreases the sulphide ion concentration
 - (b) sulphides of group IV cations are unstable in
 - (c) solubility product of group II sulphides is more than that of group IV sulphides
 - (d) presence of HCl increases the sulphide ion concentration.
- 39. The correct order of number of atoms in 1.6 g of CH₄, 1.7 g of NH₃ and 1.8 g of H₂O is

 - (a) $H_2O = NH_3 = CH_4$ (b) $H_2O < NH_3 < CH_4$
 - (c) $CH_4 < NH_3 < H_2O$ (d) $CH_4 = NH_3 < H_2O$
- **40.** How many P=O bonds are present in $(HPO_3)_3$?
 - (a) 0
- (b) 3
- (c) 6
- (d) 9

ASSERTION AND REASON

Directions: In the following questions (41-60), a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- **41. Assertion :** When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of the change.

Reason : The endothermic reactions are favoured at lower temperature and exothermic reactions are favoured by high temperature.

42. Assertion : *o*-Nitrophenol is more volatile than *p*-nitrophenol.

Reason : Intramolecular hydrogen bonding is present in *o*-nitrophenol while intermolecular H-bonding is present in *p*-nitrophenol.

43. Assertion : Lyophilic colloids are called as reversible sols.

Reason: Lyophilic sols are liquid loving.

44. Assertion : Mixture of benzaldehyde and acetaldehyde in hot alkaline medium gives cinnamaldehyde.

Reason : Benzaldehyde is a strong electrophile than acetaldehyde.

45. Assertion: Anion vacancies in alkali halides are produced by heating the alkali halide crystals with alkali metal vapour.

Reason : Electrons trapped in anion vacancies are referred to as F-centres.

46. Assertion : Hydrogen iodide cannot be prepared by the action of KI with conc. H₂SO₄.

Reason: HI has poor thermal stability in comparison to other hydrogen halides.

47. Assertion : Alkyl isocyanides in acidified water give alkyl formamides.

Reason : In isocyanides, carbon first acts as a nucleophile and then as an electrophile.

48. Assertion: van der Waals' equation is applicable only to non-ideal gases.

Reason : Ideal gases obey the equation PV = nRT.

49. Assertion: Diastereomers have different physical properties.

Reason : They are non-superimposable mirror images.

50. Assertion: Bond order can assume any value number including zero.

Reason: Higher the bond order, shorter is bond length and greater is bond energy.

51. Assertion : Colloidal silver iodide is prepared by adding silver nitrate in slight excess to potassium iodide solution. When subjected to an electric field, the colloidal particles migrate to the anode.

Reason: Colloidal particles of a particular substance always carry the same charge irrespective of the method of preparation.

52. Assertion: Rate of reaction of alkyl halides in Williamson's synthesis reaction is

 $1^{\circ}RX > 2^{\circ}RX > 3^{\circ}RX$.

Reason : It is a type of bimolecular substitution reaction $(S_N 2)$.

53. Assertion : If 30 mL of H₂ and 20 mL of O₂ react to form water, 5 mL of H₂ is left at the end of the reaction

Reason : O_2 is the limiting reagent.

54. Assertion : The formal oxidation no. of sulphur in Na₂S₄O₆ is 2.5.

Reason : Two S-atoms are not directly linked with O-atoms.

55. Assertion: For a cell reaction

 $Zn_{(s)} + Cu_{(aq)}^{2+} \rightarrow Zn_{(aq)}^{2+} + Cu_{(s)}$; at the equilibrium, voltmeter gives zero reading.

Reason : At the equilibrium, there is no change in the concentration of Cu^{2+} and Zn^{2+} ions.

56. Assertion : The position of an element in periodic table after emission of one α - and two β - particles remains unchanged.

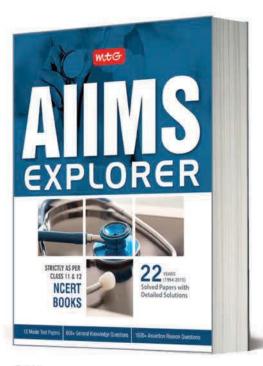
Reason : Emission of one α - and two β -particles gives isotope of the element which acquires same position in periodic table.

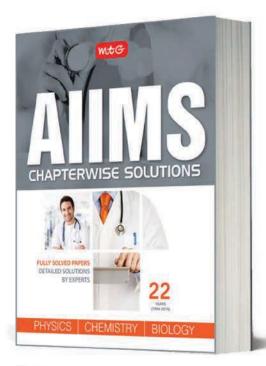
57. Assertion : The boiling point of 0.1 M urea solution is less than that of 0.1 M KCl solution.

Reason: Elevation of boiling point is directly proportional to the number of species present in the solution.



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58. Assertion :
$$(en)_2 \text{Co} (en)_2^{3+}$$
 is named

as tetrakis(ethylenediamine)- μ -hydroxo- μ -imido dicobalt (III) ion.

Reason : In naming polynuclear complexes *i.e.*, containing two or more metal atoms joined by bridging ligands, the word μ is added with hyphen before the name of such ligands.

59. Assertion: Ce⁴⁺ is used as an oxidising agent in volumetric analysis.

Reason: Ce^{3+} has the tendency to change to Ce^{4+} .

60. Assertion: K_{sp} of AB_2 salt for solubility 's' is $4s^5$. **Reason**: K_{sp} of a salt is its ionic product at any concentration.

SOLUTIONS

- (d): In S_N2 reactions, inversion of configuration occurs therefore, a single stereoisomer is produced.
 As this stereoisomer is not the enantiomer of the reactant therefore, a product with opposite sign of rotation is not necessarily produced.
- 2. (c): 2.5 g NaOH = $\frac{2.5}{40}$ equivalents of NaOH = $\left(\frac{2.5}{40} \times 1000\right)$ = 62.5 milliequivalents of NaOH Now, meq of H₂SO₄ = meq. of NaOH

Let the volume of H_2SO_4 required is V mL. or $2.5 \times 2 \times V = 62.5$ (: n-factor for $H_2SO_4 = 2$)

$$V = \frac{62.5}{5} = 12.5 \,\text{mL}$$

3. (c) : If dilution is made *V*-times molar conductance becomes *V*-times.

0.1 M $\rm H_2SO_4$ changes to 0.01 M $\rm H_2SO_4$ Thus, dilution is 100 times so, its molar conductance will be 100 times.

4. (a):
$$CH_3CH_2COOH \xrightarrow{P/Br_2} CH_3CHCOOH \xrightarrow{Br} (A) \downarrow H^+$$

$$CH_2=CH-COOH + HBr \qquad (B)$$

 $P+Br_2$ is brominating agent that brominates the α -position. The product then undergoes dehydrohalogenation in the presence of alcoholic potassium hydroxide.

- 5. (d): The structure of NO_3^- is represented as $: \ddot{O} N = \ddot{O}$.
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It has 4 bond pairs and no lone pair.

6. (b): As the slowest step is the rate determining step, hence from eq. (2),

$$r = k[O_3][O]$$

From eq. (1),
$$K_{eq} = \frac{[O_2][O]}{[O_3]}$$
 or $[O] = \frac{K_{eq}[O_3]}{[O_2]}$

Hence,
$$r = k K_{eq} \frac{[O_3]^2}{[O_2]} = k'[O_3]^2 [O_2]^{-1} [\because k' = k K_{eq}]$$

- (b): o-Nitrophenol shows intramolecular hydrogen bonding and due to chelation, it has the lowest solubility.
- 8. (d): NO \longrightarrow NO⁺ + e^- Fe²⁺ + $e^ \longrightarrow$ Fe⁺ Fe²⁺ [Ar] $3d^6$ $\downarrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$ Fe⁺ [Ar] $3d^7$ $\downarrow\uparrow\downarrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$ Three unpaired electrons $\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = 3.87 \text{ B.M.}$

9. (c):
$$Ag^+ + e^- \longrightarrow Ag$$
; $E_{Ag} = \frac{Atomic mass}{1} = 108$
Number of faradays = $\frac{W_{Ag}}{1} = \frac{108}{1} = 1$

Number of faradays =
$$\frac{W_{Ag}}{E_{Ag}} = \frac{108}{108} = 1$$

- 10. (c): $\begin{array}{c} CH_2CONH_2 \\ COOCH_3 \\ (A) \end{array}$ $\begin{array}{c} CH_2 \\ NH \\ CH_3OH \end{array}$ $\begin{array}{c} CH_2N \\ H \\ CH_3OH \end{array}$
- 11. (a): $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$
- **12. (c)**: Condensation polymerisation involves condensation reaction between two bifunctional monomers to produce dimer which in turn, produce, tetramer and so on with the loss of simple molecules like H₂O, NH₃, HCl etc.

13. (d): The structure of
$$XeO_3F_2: O = Xe O$$

No. of lone pair of Xe = 0 and no. of bond pairs = 5 Hybridisation of $Xe = sp^3d$

Hence, shape of XeO₃F₂ should be trigonal bipyramidal and not octahedral.

14. (d):
$$\underbrace{\bigcirc}_{\text{conc. HNO}_3}^{\text{conc. HNO}_3} \underbrace{\bigcirc}_{\text{FeCl}_3}^{\text{NO}_2} \underbrace{\bigcirc}_{\text{FeCl}_3}^{\text{NO}_2}$$

3-chloronitrobenzene

- 15. (d): Rate of reaction is quadrupled on doubling the concentration. Thus $r \propto [A]^2$.
- 16. (a): When mixed ethers are used, the alkyl iodide produced depends on the nature of alkyl groups. If one group is methyl and the other a primary or secondary alkyl group, then methyl iodide is produced. Here reaction occurs via S_N2 mechanism and because of the steric effect of the larger group, I⁻ attacks the smaller (Me) group.

 $CH_3OC_2H_5 + HI \longrightarrow CH_3I + C_2H_5OH$ When the substrate is a methyl *t*-alkyl ether, the products are t-RI and MeOH. Here reaction occurs by S_N1 mechanism and formation of products is controlled by the stability of carbocation. Since carbocation stability order is $3^{\circ} > 2^{\circ} > 1^{\circ} > \overset{\top}{C}H_3$, therefore alkyl halide is always derived from *tert*-alkyl group.

$$CH_{3}$$

17. (c): Relative lowering in vapour pressure,

$$\frac{p^{\circ} - p_{s}}{p^{\circ}} = \frac{w_{2}}{M_{2}} \times \frac{M_{1}}{w_{1}}$$

$$\frac{0.30 \text{ mm}}{17.54 \text{ mm}} = \frac{20}{M_{2}} \times \frac{18}{100}$$

$$\Rightarrow M_{2} = \frac{20 \times 18 \times 17.54}{0.30 \times 100} = 210.48 \approx 210.5 \text{ g}$$

19. (c): The reaction involved is called as Hofmann's bromamide reaction.

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + 2KBr + K_2CO_3$$

$$+ 2H_2O$$
Mechanism involved is:

20. (b): Average kinetic energy = $\frac{3}{2}kT$ where, k is Boltzmann constant. Average kinetic energy is the same for all gaseous molecules.

21. (b)

22. (a): Heat of hydration is higher for small sized cations. Thus, solubility of sulphates of these metals decreases down the group.

23. (d):

$$CH_3$$
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 $COOCH_3$
 - **24.** (c): CH₃CH₂CH₂CH₂OH, CH₃-CH-CH₂OH,
- **25. (b)**: Order of electronegativity is: F > O > N > C
- **26.** (a): BOD is directly proportional to the amount of organic waste which is to be decomposed. Thus, the BOD will increase.
- 27. (a):

$$CH_{2}CH=CH_{2}$$

$$+ Hg(OCOCH_{3})_{2} \rightarrow \bigcirc$$

$$CH_{2}-CH=CH_{2}$$

$$+ Hg(OCOCH_{3})$$

$$+$$

28. (d): For gas *Z*, critical temperature is highest.

$$T_c = \frac{8a}{27Rb}$$

 $\Rightarrow T_c = \frac{8 \times 12}{27 \times .0821 \times .027} = 1603.98 \text{ K}$

29. (a):
$$I_{2(s)} + H_2O_{2(aq)} + 2OH_{(aq)}^- \longrightarrow 2I_{(aq)}^- + 2H_2O_{(l)} + O_{2(aq)}$$

30. (d): It represents the condition of equilibrium hence, $\Delta G = 0$.

31. (b):
$$\pi = CRT$$

$$C = \frac{\pi}{RT} = \frac{7.8}{0.082 \times 310} = 0.31 \text{ mol/L}$$

32. (d)

33. (c): (Tropylium) carbocation contains
$$(4n + 2)\pi$$
 electrons hence, it is aromatic and most stable.

34. (a): Carnallite is an ore of potassium and its formula is KCl·MgCl₂·6H₂O.

35. (c):
$$NH_2$$

OHHN

36. (a): Energy difference between 5*f* and 6*d* orbitals is less so, actinoids have larger number of oxidation states.

37. (c):

37. (C):				
Element	%	Atomic mass	Moles of atoms	Relative Simplest ratio of atoms
С	18.5	12	$\frac{18.5}{12} = 1.542$	1
Н	1.55	1	$\frac{1.55}{1} = 1.5$	1
Cl	55.04	35.5	$\frac{55.04}{35.5} = 1.55$	1
О	24.81	16	$\frac{24.81}{16} = 1.55$	1

Therefore, empirical formula of the compound is CHClO.

38. (a)

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39. (b):

(-)-			
Molecule	No. of moles	No. of molecules	No. of Atoms
CH_4	0.1	$0.1N_{0}$	$0.5N_{0}$
NH ₃	0.1	$0.1N_{0}$	$0.4N_{0}$
H ₂ O	0.1	$0.1N_{0}$	$0.3N_{0}$

- **41. (c)**: An exothermic reaction is favoured by low temperature while an endothermic reaction is favoured by high temperature.
- **42. (a)**: *p*-Nitrophenol has higher boiling point than *o*-nitrophenol, because of intermolecular hydrogen bonding present in *p*-nitrophenol. But intramolecular hydrogen bonding in *o*-nitrophenol makes it steam volatile.
- **43. (b)**: If the dispersion medium is separated from the dispersed phase, the lyophilic sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called reversible sols.
- 44. (a): This is Claisen-Schmidt reaction.

45. (b): On heating the alkali halide crystals with alkali metal vapour the excess of alkali metal atoms deposit on the surface of the alkali halide crystal, halide ion then diffuse to the surface and combine with alkali metal atom which get ionised by losing electrons. After ionisation the alkali metal ion occupies cationic vacancy whereas electron occupies anionic vacancy.

46. (b): Hydrogen iodide cannot be prepared by the action of KI with conc. H₂SO₄ because H₂SO₄ oxidises HI to I₂.

$$\mathrm{H_2SO_4} + 2\mathrm{HI} \longrightarrow \mathrm{I_2} + \mathrm{SO_2} + 2\mathrm{H_2O}$$

47. (a): In an isocyanide, first an electrophile and then a nucleophile add at the carbon to form a species which usually undergoes further transformations.

$$R\overset{+}{\mathbf{N}} \equiv C^{-} + E^{+} \longrightarrow R\overset{+}{\mathbf{N}} \equiv CE \xrightarrow{\mathbf{N}\mathbf{u}^{-}} R\mathbf{N} \equiv C(\mathbf{N}\mathbf{u})E$$

 $R\overset{+}{\mathbf{N}} \equiv C^{-} + \mathbf{H}_{2}\mathbf{O} \longrightarrow R\mathbf{N} \equiv CHOH \longrightarrow R\mathbf{N}HCHO$
Alkyl formamide

- 48. (b): In real gases, the intermolecular forces of attraction and the volume occupied by the gas molecules cannot be neglected.
- 49. (c): Stereoisomers which are not mirror images of each other are called diastereomers. They have similar chemical properties because they belong to the same family, but they do not have identical physical properties because of difference in their relative configurations.
- **50. (b):** Bond order = $\frac{1}{2}(N_b N_a)$.

Bond order zero indicates that the bond does not exist.

- 51. (d): As AgNO₃ is in excess, the AgI particles will adsorb Ag⁺ ions and move towards cathode. Colloidal particles of AgI may be positively or negatively charged depending upon whether AgNO₃ is in excess or KI is in excess.
- **52.** (a): Williamson's synthesis occurs by $S_N 2$ mechanism and primary alkyl halides are most reactive in S_N 2 reactions.

53. (d):
$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

 $_{30 \text{ mL}}$ $_{15 \text{ mL reacted}}$

Volume of O_2 left = 20 – 15 = 5 mL Since H₂ is completely consumed, hence, it is the limiting reagent.

54. (a):
$$\overset{+}{N}a\overset{-}{O} - \overset{O}{\overset{||_{+5}}{S}} \overset{0}{-} \overset{0}{\overset{||_{+5}}{S}} \overset{-}{\overset{-}{S}} \overset{-}{\overset{-}{O}} \overset{+}{\overset{-}{N}a}$$

Formal oxidation number of sulphur

$$=\frac{2\times5+2\times0}{4}=2.5$$

55. (a): $Zn_{(s)} + Cu_{(aq)}^{2+} \rightarrow Zn_{(aq)}^{2+} + Cu_{(s)}$

As the time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu²⁺ keeps on decreasing. At the same time voltage of the cell keeps on decreasing. When there is no change in concentration of Cu²⁺ and Zn²⁺ ions, voltmeter gives zero reading and this state is known as equilibrium.

- **56.** (a): The loss of one α -particle will reduce the mass number by four and atomic number by two. Subsequent two β-emissions will increase the atomic number by two without affecting the mass number. Hence, the new element will be only an isotope of the parent atom and hence its position in the periodic table remains unchanged.

58. (a):
$$[(en)_2 \text{Co}]^{3+}$$
 is named as

tetrakis(ethylenediamine)-µ-hydroxo-µ-imido dicobalt (III) ion. For more than one bridging group the word μ is repeated before each bridging group.

- **59.** (c): Ce^{4+} has the tendency to change to Ce^{3+} (as +3) oxidation state is more stable).
- **60.** (d): K_{sp} for $AB_2 = 4s^3$ K_{sp} equals ionic product in saturated solution.

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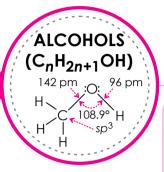
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ALCOHOLS, PHENOLS AND ETHERS

Alcohols, phenols and ethers are the basic in day-to-day life.

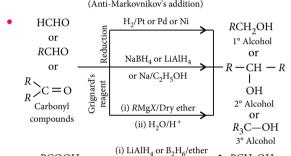


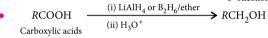
B.pt.
$$\infty$$
 No. of C-atoms ∞ $\frac{1}{Branching}$
Solubility ∞ $\frac{1}{Size}$ ∞ Branching



Preparation









Physical properties

- Pure phenols are colourless liquids or solids.
- Form intermolecular hydrogen bonds hence, soluble in water.

Preparation

$$\begin{array}{c} \bullet \quad \text{C_6H}_5\text{SO}_3\text{H} \quad \frac{\text{NaOH}}{-\text{H}_2\text{O}} \hspace{-0.1cm} \hspace{$$



Classification

- Simple or symmetrical: Same alkyl groups are attached to
- Mixed or unsymmetrical: Different alkyl groups are attached to oxygen, ROR'.
- **Aliphatic ethers**: *R* and *R'* both are alkyl groups.
- **Aromatic ethers:** Either one or both R and R' are anyl groups.

Chemical properties

$$ROR + HCl(conc.)$$
 \longrightarrow $\begin{bmatrix} R \\ P \\ Cl \end{bmatrix} - H Cl$

Cleavage of C - O bond:

$$R - OR + HX \xrightarrow{373 \text{ K}} R - OH + R - X$$

- In case of alkyl aryl ethers, phenol and an alkyl halide are obtained.

$$ROR + H_2O \xrightarrow{\text{dil. } H_2SO_4} 2R - OH$$

$$ROR + PCl_5 \xrightarrow{\Delta} 2R - Cl$$

Reactions involving alkyl group:

alkoxy group (-OR).

- Formation of peroxides with air and light.
- Substitution products obtained on halogenation.
- Electrophilic substitution reactions: Aryl alkyl ethers give o- and p-substituted products due to +R effect of

compounds of organic chemistry and they find wide applications in industry as well as

Chemical properties

- Cleavage of O—H bond: Ease of reaction depends on stability of alkoxide ion.
 - Acidity: Phenols > Water > 1° alcohol > 2° alcohol > 3° alcohol
- Cleavage of C—OH bond: Ease of reaction depends on stability of carbocations.

Order of reactivity: 3° alcohol > 2° alcohol > 1° alcohol

Reactions involving whole alcohol molecule:

Reactions involving whole alcohol molecule:

Dehydration:
$$R-OH+conc. H_2SO_4 \xrightarrow{443 \text{ K}} > C = C <$$

$$R-OH+Al_2O_3 \xrightarrow{513 \text{ K}} ROR$$

$$R-OH+Al_2O_3 \xrightarrow{633 \text{ K}} > C = C <$$

Oxidation: Alcohol Oxidation: Alcohol Carboxylic acid

Dehydrogenation :1° alcohol Cu/273 K → Aldehyde

2° alcohol Cu/273 K ★ Ketone

Dehydration: 3° alcohol $\xrightarrow{\text{Cu/273 K}}$ C=C

Distinction tests

- **Dichromate test (oxidation) :** 1° alcohol \rightarrow Acid with same number of C-atoms; 2° alcohol → Ketone with same number of C-atoms; 3° alcohol \rightarrow No reaction under normal conditions.
- Victor Meyer's test: 1° alcohol → Blood red colour; 2° alcohol → Blue colour; 3° alcohol → Colourless.
- **Lucas test :** 1° alcohol \rightarrow No turbidity; 2° alcohol \rightarrow Turbidity in 5 minutes; 3° alcohol → Turbidity appears immediately.

Some important alcohols

- Methanol: Prepared by catalytic hydrogenation of carbon monoxide or water gas. It is used as a solvent, preservative, substitute for petrol, etc.
- **Ethanol:** Prepared by the hydration of ethene or by the fermentation of molasses. It is used as an antiseptic, power alcohol, in beverages, etc.

Chemical properties

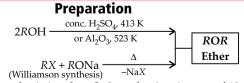
Electrophilic substitution of phenols: Halogenation, sulphonation, nitration, Friedel-Crafts alkylation, etc. occur at o- and p- positions due to activating effect of —OH group.

Tests to distinguish phenols from alcohols

- FeCl₃ test: Gives violet colour
- Br₂ H₂O test : Gives white ppt.
- Liebermann's nitroso test: Gives blue colour which turns red on
- Ammonia/Sodium hypochlorite test: Gives blue colour
- Azo dye test: Gives orange colour

Physical properties

- Dipolar due to slightly polar C—O bonds.
- B.pts. are lower than isomeric alcohols due to lack of hydrogen
- Solubility in water $\propto \frac{1}{\text{Molecular mass}}$ (soluble due to formation of H-bonds with water)
- Fairly soluble in organic solvents.
- Lighter than water.



- Williamson synthesis involves $S_{\mbox{\scriptsize N}}2$ mechanism in case of 1° alkyl
- In the case of 2° and 3° alkyl halides, elimination takes place.
- Dehydration of alcohols for the formation of ethers follows the order:

Uses

Ethers are used as industrial solvents, heat transfer medium (diphenyl ether), flavouring agents and in perfumes.

PRACTICE PAPER

Exam date : 2 14th to 28th May 2016

- 1. The chemical name of aspirin is
 - (a) methyl salicylate
- (b) acetylsalicylic acid
- (c) sodium salicylate
- (d) salicylic acid.
- **2.** The half life period of radon is 3.8 days. After how many days will only one-twentieth of radon sample be left over?
 - (a) 8.54 days
- (b) 20 days
- (c) 11.28 days
- (d) 16.46 days
- 3. Which of the following acts as a sink for CO?
 - (a) Plants
 - (b) Haemoglobin
 - (c) Microorganisms present in the soil
 - (d) Oceans
- **4.** The plot of $1/x_A$ versus $1/y_A$ (where x_A and y_A are the mole fractions of A in liquid and vapour phases respectively) is linear whose slope and intercept respectively are given as
 - (a) $\frac{p^{\circ}_{A}}{p^{\circ}_{B}}$, $\frac{(p^{\circ}_{A} p^{\circ}_{B})}{p^{\circ}_{B}}$ (b) $\frac{p^{\circ}_{A}}{p^{\circ}_{B}}$, $\frac{(p^{\circ}_{B} p^{\circ}_{A})}{p^{\circ}_{B}}$
 - (c) $\frac{p^{\circ}_{B}}{p^{\circ}_{A}}$, $\frac{(p^{\circ}_{A} p^{\circ}_{B})}{p^{\circ}_{B}}$ (d) $\frac{p^{\circ}_{B}}{p^{\circ}_{A}}$, $\frac{(p^{\circ}_{B} p^{\circ}_{A})}{p^{\circ}_{B}}$
- 5. The standard reduction potentials of Pb and Zn electrodes are -0.126 and -0.763 volts respectively. The cell equation will be
 - (a) $Pb^{2+} + Zn \rightarrow Pb + Zn^{2+}$
 - (b) $Pb + 2Zn^{2+} \rightarrow Pb^{4+} + 2Zn$
 - (c) $Zn^{2+} + Pb \rightarrow Zn + Pb^{2+}$
 - (d) none of the above.
- 6. Colourless solutions of the following four salts are placed separately in four different test tubes and a strip of copper is dipped in each one of these. Which solution will turn blue?
 - (a) KNO₃
- (b) AgNO₃
- (c) $Zn(NO_3)_2$
- (d) $ZnSO_4$

- 7. Amongst H₂O, H₂S, H₂Se and H₂Te, the one with the highest boiling point is
 - (a) H₂O because of hydrogen bonding
 - (b) H₂Te because of higher molecular weight
 - (c) H₂S because of hydrogen bonding
 - (d) H₂Se because of lower molecular weight.
- **8.** Of the following statements about enzymes which is/are true?
 - (i) Enzymes lack in nucleophilic groups.
 - (ii) Enzymes are highly specific both in binding chiral substrates and in catalysing their reactions.
 - (iii) Enzymes catalyse chemical reactions by lowering the energy of activation.
 - (iv) Pepsin is a proteolytic enzyme.
 - (a) (i) and (iv)
- (b) (i) and (iii)
- (c) (ii), (iii) and (iv)
- (d) (i) only
- **9.** Bakelite is made from phenol and formaldehyde. The initial reaction between them is the example of
 - (a) electrophilic aromatic substitution
 - (b) nucleophilic aromatic substitution
 - (c) free radical reaction
 - (d) aldol reaction.
- **10.** Carbylamine test is performed in alcoholic KOH by heating a mixture of
 - (a) chloroform and silver powder
 - (b) trihalogenated methane and a primary amine
 - (c) an alkyl halide and a primary amine
 - (d) an alkyl cyanide and a primary amine.
- 11. When chlorine water is added to an aqueous solution of potassium halide in presence of chloroform, a violet colour is obtained. On adding more of chlorine water, the violet colour disappears, and a colourless solution is obtained. This test confirms the presence of _____ in aqueous solution.
 - (a) iodide
- (b) bromide
- (c) chloride
- (d) iodide and bromide

- 12. Which of the following statements is incorrect?
 - (a) Brownian movement and Tyndall effect are shown by colloidal systems.
 - (b) Gold number is a measure of the protective power of a lyophillic colloid.
 - (c) The colloidal solution of a liquid in liquid is called gel.
 - (d) Hardy-Schulze rule is related with coagulation.
- 13. The reaction given below, involving the gases is observed to be first order with rate constant $7.48 \times 10^{-3} \text{ sec}^{-1}$. Calculate the time required for the total pressure (in a system containing A at an initial pressure of 0.1 atm) to rise to 0.145 atm and also, find the total pressure after 100 sec.

$$2A_{(g)} \rightarrow 4B_{(g)} + C_{(g)}$$

- (a) 46.5 sec, 0.12 atm
- (b) 47.7 sec, 0.18 atm
- (c) 50.2 sec, 0.16 atm
- (d) None of these
- **14.** If a refrigerator's door is kept opened, then
 - (a) room gets cooled
 - (b) room gets heated
 - (c) more heat is passed out
 - (d) there is no effect.
- 15. The pH of pure water at 25°C and 35°C are 7 and 6 respectively. The heat of formation of water from H⁺ and OH⁻ is
 - (a) 64.55 kcal/mol
- (b) 74.55 kcal/mol
- (c) 84.55 kcal/mol
- (d) -54.55 kcal/mol
- **16.** The oxide which is used as white pigment is
 - (a) ZnO
- (b) FeO
- (c) NiO
- (d) CuO
- 17. Stearic acid, C₁₇H₃₅COOH has a density of 0.85 g/cm³. The molecule occupies an area of 0.205 nm² in a closed packed surface film. Calculate the length of the molecule.
 - (a) 3.8073 nm
- (b) 8.3073 nm
- (c) 2.7073 nm
- (d) 1.8073 nm
- **18.** An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralize 10 mL of this solution is
- (a) 40 mL (b) 20 mL (c) 10 mL (d) 4 mL
- 19. The pair of structures given below represent

- (a) enantiomers
- (b) diastereomers
- (c) structural isomers
- (d) two molecules of the same compound.
- 20. Which among the following statements are true for
 - (1) It exists in crystalline form.
 - (2) It is optically active.
 - (3) It is soluble in water.
 - (4) It can form zwitter ion.
 - (a) 1, 2 and 3
- (b) 1, 2 and 4
- (c) 1, 3 and 4
- (d) 2, 3 and 4
- 21. Lemon juice normally has a pH of 2. If all the acid in the lemon juice is citric acid and there are no citrate salts present, then what will be the citric acid concentration (H.Cit) in the lemon juice? (Assume that only the first hydrogen of citric acid is important). (H.Cit \Longrightarrow H⁺ + Cit⁻; $K_a = 8.4 \times 10^{-4} \text{ mol lit}^{-1}$)
 - (a) $8.4 \times 10^{-4} \text{ M}$
- (b) $4.2 \times 10^{-4} \,\mathrm{M}$
- (c) $16.8 \times 10^{-4} \text{ M}$
- (d) $12.0 \times 10^{-2} \text{ M}$
- 22. The dissociation energy of H₂ is 430.53 kJ mol⁻¹. If hydrogen is dissociated by illumination with radiation of wavelength 253.7 nm, the fraction of the radiant energy which will be converted into kinetic energy is given by
 - (a) 100% (b) 8.78%
- (c) 2.22% (d) 1.22%
- **23.** For which of the following reactions ΔH is less than
 - (a) $HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$
- 24. Two students performed the same experiment separately and each one of them recorded two readings of mass which are given below. Correct reading of mass is 5.0 g. On the basis of given data, mark the correct option out of the following statements.

Students Readings (i) (ii) A5.01 4.99 В 5.05 4.95

- (a) Results of both the students are neither accurate nor precise.
- (b) Results of student A are both precise and accurate.
- (c) Results of student B are neither precise nor
- (d) Results of student B are both precise and accurate.

25. In the given reaction,

O

$$CH_3 - C - CH_3 \xrightarrow{SeO_2} X + Se + H_2O$$
,
X is
O O O
(a) $CH_3 - C - C - H$ (b) $CH_3 - C - OCH_3$

- (c) $CH_3 C CH_2OH$ (d) none of these.
- **26.** In which isomer of C₇H₇NO₂ there are two functional groups?
 - (a) Phenyl nitromethane (b) *m*-nitrotoluene
 - (c) Anthranilic acid
- (d) Benzyl nitrite
- 27. Which of the following is not correct representation of first law of thermodynamics?
 - (a) Isochoric process; $\Delta E = q$
 - (b) Isothermal process; q = -w
 - (c) Adiabatic process; q = -w
 - (d) Cyclic process; q = -w
- 28. The incorrect statement among the following is
 - (a) the first ionization potential of Al is less than the first ionization potential of Mg
 - (b) the second ionization potential of Mg is greater than the second ionization potential of Na
 - (c) the first ionization potential of Na is less than the first ionization potential of Mg
 - (d) the third ionization potential of Mg is greater than the third ionization potential of Al.
- 29. In presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikoff's addition to alkenes because
 - (a) both are highly ionic
 - (b) one is oxidising and the other is reducing
 - (c) one of the step is endothermic in both the cases
 - (d) all the steps are exothermic in both the cases.
- 30. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
 - (a) benzyl alcohol and sodium formate
 - (b) sodium benzoate and methyl alcohol
 - (c) sodium benzoate and sodium formate
 - (d) benzyl alcohol and methyl alcohol.
- 31. The increase in the molar conductivity of HCl with dilution is due to
 - (a) increase in the self ionisation of water
 - (b) decrease in the self ionisation of water
 - (c) decrease in the interionic forces
 - (d) none of these.

32. Trimethylamine is a pyramidal molecule

hybridisations of nitrogen in both are __ and __ respectively.

- (a) sp^2, sp^2
- (b) sp^3 , sp^2 (d) sp^2 , sp
- (c) sp^{3} , sp^{3}
- 33. Which of the following processes will convert starch directly into glucose?
 - (a) Heating with dilute H₂SO₄.
 - (b) Fermentation by diastase.
 - (c) Fermentation by zymase.
 - (d) Heating with dilute NaOH.
- **34.** PbF_4 , $PbCl_4$ exist but $PbBr_4$ and PbI_4 do not exist
 - (a) large size of Br⁻ and I⁻
 - (b) strong oxidising character of Pb⁴⁺
 - (c) strong reducing character of Pb⁴⁺
 - (d) low electronegativity of Br⁻ and I⁻.
- 35. Match list I with list II and select the correct answer using the codes given below:

	_	
	List I	List II
	(Reactions)	(Products)
(P)	(CH ₃) ₂ NH	I. O
	+C ₆ H ₅ COCl	$(CH_3)_2N - \stackrel{\parallel}{\stackrel{\square}{\stackrel{\square}{\stackrel{\square}{\stackrel{\square}{\stackrel{\square}{\stackrel{\square}{\stackrel{\square}{$
(0)		0
(Q)	2CH ₃ CH ₂ NH ₂	II.
	O	
	+ <u>O</u>	
	Ö	
(R)	$(CH_3)_2NH +$	III.
	SO ₂ Cl	C ₂ H ₅ NHCO(CH ₂) ₂ COO
		$+ C_2H_5\overset{T}{N}H_3$
(S)	СНО +	IV.
	\sim NH ₂	$(CH_3)_2N-C$

II

Codes:

(d) IV

P	Q	R	S
(a) III	IV	I	II
(b) IV	III	II	I
(c) I	II	III	IV

Ш

- **36.** An alkyl halide with molecular formula, $C_6H_{13}Br$ on treatment with alcoholic KOH gave two isomeric alkenes, A and B. Reductive ozonolysis of the mixture gave the following compounds: CH₃COCH₃, CH₃CHO, CH₃CH₂CHO (CH₃)₂CHCHO. The alkyl halide is
 - (a) 2-bromohexane
 - (b) 3-bromo-2-methylpentane
 - (c) 2,2-dimethyl-1-bromobutane
 - (d) 2-bromo-2, 3-dimethylbutane.
- **37.** Anhydride of nitric acid is
 - (a) N_2O
- (b) NO₂
- (c) N_2O_5 (d) N_2O_3
- 38. How many grams of sucrose (mol. wt. = 342) should be dissolved in 100 g water in order to produce a solution with a 105.0°C difference between the freezing and the boiling temperatures?

(
$$K_f = 1.86^{\circ}$$
 C/m, $K_b = 0.51^{\circ}$ C/m)
(a) 34.2 g (b) 72 g (c) 342 g (d) 460 g

- 39. The lower boiling point of helium is due to its
 - (a) inertness
- (b) gaseous nature
- (c) high polarisability
- (d) weak van der Waals forces between atoms.
- 40. The correct order of basicity of the following

. The correct order of basicity of compounds is
$$\begin{array}{ccc} \text{CH}_3\text{-}\text{C} & \text{NH} \\ \text{CH}_3\text{-}\text{C} & \text{NH}_2 \\ \text{(I)} & \text{CH}_3\text{-}\text{CH}_2\text{-}\text{NH}_2 \\ \text{(CH}_3)_2\text{NH} & \text{(II)} \\ \text{(III)} & \text{CH}_3\text{-}\text{C}\text{-}\text{NH}_2 \\ \text{(IV)} \end{array}$$

- (a) II > I > III > IV
- (b) I > III > II > IV
- (c) III > I > II > IV
- (d) I > II > III > IV

SOLUTIONS

1. (b): Structural formula of aspirin is



IUPAC name: 2-Acetoxybenzoic acid Chemical name: Acetylsalicylic acid

(d): We know that, $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.8} = 0.182 \text{ day}^{-1}$

Let the initial amount of radon be N_0 and the amount left after t days be N which is equal to $\frac{N_0}{20}$ Applying the equation,

$$t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$$

$$= \frac{2.303}{0.182} \log_{10} \frac{N_0}{N_0 / 20} = \frac{2.303}{0.182} \log_{10} 20$$

$$= 16.46 \text{ days}$$

- (c): CO is converted into CO₂ by microorganisms present in soil.
- **(b)**: $P_A = x_A p_A^{\circ}$, $P_B = x_B p_B^{\circ}$

(b):
$$P_A = x_A p_A^{\circ}$$
, $P_B = x_B p_B^{\circ}$

$$y_A = \frac{p_A}{p_A + p_B} = \frac{x_A p_A^{\circ}}{x_A p_A^{\circ} + x_B p_B^{\circ}}$$

$$= \frac{x_A p_A^{\circ}}{x_A p_A^{\circ} + (1 - x_A) p_B^{\circ}} = \frac{x_A p_A^{\circ}}{x_A (p_A^{\circ} - p_B^{\circ}) + p_B^{\circ}}$$
or, $\frac{1}{y_A} = \frac{x_A (p_A^{\circ} - p_B^{\circ}) + p_B^{\circ}}{x_A p_A^{\circ}}$

or,
$$\frac{y_A}{y_A} = \frac{x_A p_A^{\circ}}{x_A p_A^{\circ}}$$

or, $\frac{1}{y_A} = \frac{p_A^{\circ} - p_B^{\circ}}{p_A^{\circ}} + \frac{p_B^{\circ}}{p_A^{\circ}} \frac{1}{x_A}$

or,
$$\frac{1}{r_{+}} = \frac{p_{A}^{\circ}}{p_{A}^{\circ}} + \frac{p_{A}^{\circ}}{p_{A}^{\circ}} + \frac{p_{B}^{\circ}}{p_{A}^{\circ}} $

or,
$$\frac{1}{x_A} = \frac{p_A^{\circ}}{p_B^{\circ}} \frac{1}{y_A} + \frac{p_B^{\circ} - p_A^{\circ}}{p_B^{\circ}}$$
Hence, plot of
$$\frac{1}{x_A} vs \frac{1}{y_A} \text{ will be linear with}$$

$$slope = \frac{p_A^{\circ}}{p_B^{\circ}} \text{ and intercept} = \frac{(p_B^{\circ} - p_A^{\circ})}{p_B^{\circ}}.$$

- (a): The E°_{red} of Zn is lower than that of Pb, hence Zn is a better reducing agent than Pb.
 - :. The correct cell reaction will be $Pb^{2+} + Zn \rightarrow Pb + Zn^{2+}$
- (b): As Cu is more reactive than Ag.

 $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$

Cu²⁺ will give blue solution. Cu is below in electrochemical series than K and Zn hence, no reaction takes place with KNO₃, Zn(NO₃)₂ and

- (a): H2O has the highest boiling point due to H-bonding.
- 8.
- (a): The reaction of phenol and formaldehyde is called Lederer Manasse reaction. It follows electrophilic addition and rearrangement mechanism.

$$CH_2 = O + H^+ \longrightarrow CH_2OH$$

10. (b): Trihalogenated methane (CHX_3) and a primary amine, i.e.;

$$CHX_3 + RNH_2 + 3KOH \rightarrow RNC + 3KX + 3H_2O$$

11. (a): $2I^- + Cl_2 \longrightarrow I_2 + 2Cl^-$

$$5Cl_2 + I_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$$

Excess Colourless

- 12. (c): Liquid-liquid system is known as emulsion.
- 13. (b): $2A_{(g)} \rightarrow 4B_{(g)} + C_{(g)}$ Initial: $P_0 \qquad 0 \qquad 0$

At time: $t P_0 - P' 2P' P'/2$

time:
$$t = P_0 - P' = 2P' = P/2$$

$$P_{\text{total}} = P_0 - P' + 2P' + P'/2 = P_0 + \frac{3P'}{2}$$

$$P' = \frac{2}{3}(P_{\text{total}} - P_0)$$

$$P' = \frac{2}{3}(0.145 - 0.1) = 0.03 \text{ atm}$$

$$K = \frac{2.303}{t} \log \frac{P_0}{P_0 - P'}$$

$$t = \frac{2.303}{7.48 \times 10^{-3}} \log \frac{0.1}{0.07} = 47.7 \text{ sec}$$

Also,
$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - P'}$$

$$k = \frac{2.303}{100} \log \left(\frac{0.1}{0.1 - P'} \right)$$

$$\Rightarrow$$
 0.1 - $P' = 0.047$ or $P' = 0.053$

$$P_{\text{total}} = 0.1 + \frac{3}{2} (0.053) \approx 0.18 \text{ atm}$$

- 14. (b): The room gets heated because to maintain the cooling inside the refrigerator its radiator radiates heat to the surroundings continuously.
- **15.** (c): At 25°C, $[H^+] = 10^{-7}$. $K_{w_1} = 10^{-14}$ At 35°C, [H⁺] = 10^{-6} . $K_{w_2} = 10^{-12}$

Now using, $2.303 \log \frac{K_{w_2}}{K} = \frac{\Delta H}{R} \left| \frac{T_2 - T_1}{T_1 \times T_2} \right|$

$$2.303 \log \frac{10^{-12}}{10^{-14}} = \frac{\Delta H}{2} \left[\frac{10}{298 \times 308} \right]$$

 $\Delta H = 84551.4 \text{ cal/mol} = 84.551 \text{ kcal/mol}$

Thus, $H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H = 84.551$ kcal/mol

$$\therefore$$
 H⁺ + OH⁻ \rightleftharpoons H₂O; $\Delta H = -84.551$ kcal/mol

- 16. (a): ZnO is used in white paints in place of white lead. It does not get blackened with hydrogen sulphide present in air as the white lead paint does. It is also known as Philosopher's wool.
- 17. (c): Molar mass of stearic acid = 284

Mass of one molecule =
$$\frac{284}{6.02 \times 10^{23}}$$
 g

Volume of one molecule =
$$\frac{284}{6.02 \times 10^{23} \times 0.85}$$
$$= 55.5 \times 10^{-23} \text{ cm}^{-2}$$

Area occupied by the molecule = 0.205 nm^2

$$= 0.205 \times 10^{-18} \text{ m}^2 = 0.205 \times 10^{-14} \text{ cm}^2$$

Hence, length of the molecule = $\frac{\text{volume}}{\text{area}}$

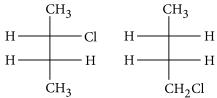
$$= \frac{55.5 \times 10^{-23}}{0.205 \times 10^{-14}} = 270.73 \times 10^{-9} \text{ cm} = 2.7073 \text{ nm}$$

18. (a): Normality of oxalic acid = $\frac{6.3 \times 1000}{63 \times 250}$ = 0.4 N

$$N_1V_1=N_2V_2$$
 or $0.1\times V_1=0.4\times 10$

$$\therefore V_1 = 40 \text{ mL}$$

19. (c): Convert these Newmann projections into open chain structures.



Both structures have same molecular formula C_4H_9Cl , thus these are isomers. However, the two have different groups, viz CH₃ and CH₂Cl, so these are neither enantiomers nor diastereomers. Hence, these are structural isomers.

21. (d):
$$K_a = \frac{[H^+][\text{cit}^-]}{[H. \text{cit}]}$$

$$8.4 \times 10^{-4} = \frac{[10^{-2}][10^{-2}]}{[H. cit]}$$

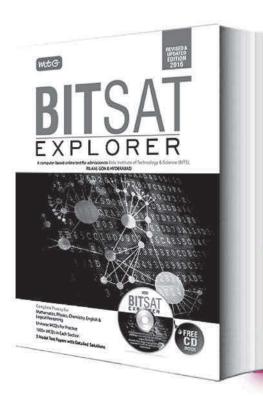
$$8.4 \times 10^{-4} = \frac{10^{-4}}{[\text{H. cit}]}$$

[H. cit] =
$$\frac{10^{-4}}{8.4 \times 10^{-4}} = 0.119$$

= $11.9 \times 10^{-2} \text{ M} \approx 12 \times 10^{-2} \text{ M}$



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Available at all leading book shops throughout the country. To buy online visit www.mtg.in. For more information or for help in placing your order, call 0124-6601200 or e-mail info@mtq.in 22. (b): Energy of 1 mole of photons,

$$E = N_0 h \upsilon = \frac{N_0 \times h \times c}{\lambda}$$

Energy converted into K.E. = (472 - 430.53) kJ % of energy converted into K.E.

$$=\frac{(472-430.53)}{472}\times100=8.78\%$$

23. (d): $\Delta n = 2 - 4 = -2$ $\therefore \Delta H = \Delta E + (-2)RT \text{ or, } \Delta H = \Delta E - 2RT$

Hence, $\Delta H < \Delta E$

- **24. (b)**: Results of student *B* is accurate but not precise.
- **25.** (a): SeO₂ oxidises compounds containing active methylene group (*i.e.* CH₂ next to the carbonyl group) to another CO group. *i.e.*,

$$CH_3 - C - CH_3 \xrightarrow{SeO_2} CH_3 - CH_3 - CHO + Se + H_2O$$

26. (c):
$$\begin{array}{c} \text{COOH} \\ \text{Anthranilic acid} \end{array}$$

- 27. (c): For adiabatic process, q = 0; so, $\Delta E = w$
- **28. (b)**: *IE*₂ of Mg is lower than that of Na because in case of Mg⁺, one *s*-electron has to be removed where in case of Na⁺, an electron is to be removed from the stable inert gas configuration which is difficult.
- **29.** (c): One of the steps, (*i.e.* the reaction of HCl with carbon radical in case of HCl and addition of iodine radical to double bond in case of HI) is endothermic in both the cases.
- **30.** (a): A mixture of benzaldehyde and formaldehyde undergoes cross Cannizzaro reaction.

$$C_6H_5CHO + HCHO \xrightarrow{\text{NaOH}} C_6H_5CH_2OH + HCOONa$$

- **31. (c)**: Due to increase in volume of water, interionic forces of HCl will decrease. Hence, ionic mobility will increase and consequently, the molar conductivity will also increase.
- 32. (b): In amine, the nitrogen is sp^3 hybridised and in amide, the nitrogen is sp^2 hybridised.
- 33. (a): Fermentation by diastase will convert starch into maltose but not into glucose. Zymase does not affect starch. Further, dilute NaOH will not hydrolyse starch because the various glucose units in it are linked to each other by glycosidic linkages which are resistant to hydrolysis by NaOH. Thus, only dilute H₂SO₄ will hydrolyse starch into glucose.

- **34. (b):** F₂ and Cl₂ are more oxidising in nature hence, they can form Pb in + 4 oxidation state but Br₂ and I₂ cannot. Secondly, Pb⁴⁺ is strong oxidising agent and in its presence Br⁻ and I⁻ cannot exist.
- 35. (d)
- **36. (b):** Out of CH₃COCH₃, CH₃CHO, CH₃CH₂CHO and (CH₃)₂CHCHO, two pairs containing a total of six carbon atoms are :
 - (i) CH₃COCH₃ + CH₃CH₂CHO
 - (ii) CH₃CHO + (CH₃)₂CHCHO

The alkenes which will give these pairs of compounds on ozonolysis are:

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \end{array} \begin{array}{c} \text{C=CHCH}_{2}\text{CH}_{3} \\ \text{2-Methyl-2-pentene} \end{array}$$
 and
$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \end{array} \begin{array}{c} \text{CH-CH=CHCH}_{3} \\ \text{4-Methyl-2-pentene} \end{array}$$

These two alkenes can be obtained as dehydrogenation products if the alkyl halide is

- 37. (c): $2HNO_3 \xrightarrow{P_2O_5} N_2O_5 + H_2O$
- 38. (b): Boiling point $(T_b) = 100 + \Delta T_b = 100 + K_b m$ Freezing point $(T_f) = 0 - \Delta T_f = -K_f m$ $T_b - T_f = (100 + K_b m) - (-K_f m)$ 105 = 100 + 0.51 m + 1.86 m

2.37
$$m = 5$$
 or, $m = \frac{5}{2.37} = 2.11 \text{ m}$

- .. Wt. of sucrose to be dissolved in 100 g water $= \frac{2.11 \times 342}{1000} \times 100 = 72 \text{ g}$
- **39.** (d): Due to weak van der Waals forces, He has lowest boiling point.

40. (b):
$$CH_3 - \overset{NH}{C} - NH_2 + H^+ \longrightarrow CH_3 - \overset{N}{C} - NH_2$$
 $\stackrel{NH}{\longrightarrow} CH_3 - \overset{NH}{C} - NH_2 \longleftrightarrow CH_3 - \overset{NH}{C} = \overset{N}{N}H_2$
 $\stackrel{NH}{\longrightarrow} CH_3 - C - NH_2 \longleftrightarrow CH_3 - C = \overset{N}{N}H_2$

The conjugate acid obtained by addition of a proton to I is stabilised by two equivalent resonance structures and hence, compound I is the most basic. Further 2° amines are more basic than 1° amines while amides are least basic due to delocalization of lone pair of electrons of N over the CO group. Thus the order is: I > III > IV



- 1. Mass of one ${}^{14}_{7}$ N atom is
 - (a) 14 amu
- (b) 7 amu
- (c) 14 g
- (d) 7 g
- The incorrect IUPAC name is

O
$$CH_3$$
 || | | (a) $CH_3 - C - CH - CH_3$ 2-Methylbutan-3-one

(b)
$$CH_3 - CH - CH - CH_3$$

 $CH_3 - CH_2CH_3$

(c)
$$CH_3 - C \equiv C - CH(CH_3)_2$$
4-Methylpent-2-yne

- 3. Choose the correct statement.
 - (a) Saccharin is 650 times sweeter than sucrose.
 - (b) Aspartame is 550 times sweeter than sucrose.
 - (c) Sucralose is 160 times sweeter than sucrose.
 - (d) Alitame is 2000 times sweeter than sucrose.
- 4. Which of the following represents the correct order of boiling points of the given substances?
 - (a) *n*-pentane > isopentane > neopentane
 - (b) isopentane > neopentane > n-pentane
 - (c) neopentane > n-pentane > isopentane
 - (d) *n*-pentane > neopentane > isopentane
- **5.** For the non-stoichiometric reaction :

 $2A + B \rightarrow C + D$, the following kinetic data was obtained in three separate experiments, all at 298 K.

Initial concentration	Initial concentration	Initial rate of formation of
[A]	[B]	$C \pmod{L^{-1}s^{-1}}$
0.1 M	0.1 M	1.2×10^{-3}
0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of *C* is

(a)
$$\frac{dC}{dt} = k[A]$$

(b)
$$\frac{dC}{dt} = k[A][B]$$

(c)
$$\frac{dC}{dt} = k[A]^2 [B$$

(a)
$$\frac{dC}{dt} = k[A]$$
 (b) $\frac{dC}{dt} = k[A][B]$
(c) $\frac{dC}{dt} = k[A]^2[B]$ (d) $\frac{dC}{dt} = k[A][B]^2$

6. For the cell reaction,

$$Cu_{(s)} + Cl_{2(g)} \longrightarrow Cu_{(aq.)}^{2+} + 2Cl_{(aq.)}^{-}$$

Cell notation is

- (a) $Cu_{(s)}|Cu_{(aq.)}^{2+}||Cl_{(aq.)}^{-}|Cl_{2(g)}|C_{(s)}$
- (b) $C_{(s)}|Cl_{(aq.)}^-|Cl_{2(g)}||Cu_{(aq.)}^{2+}|Cu_{(s)}^-|$
- (c) $Cu_{(s)}|Cu_{(aq.)}^{2+}||Cl_{(aq.)}^{-}|Cl_{2(g)}$
- (d) $Cu_{(s)}|Cu_{(aq.)}^{2+}||Cl_{2(g)}|Cl_{(aq.)}^{-}$
- Aniline in a set of reactions yielded a product *D*.

The product *D* would be

- (a) $C_6H_5CH_2NH_2$
- (b) C₆H₅NHCH₂CH₃
- (c) C_6H_5NHOH
- (d) $C_6H_5CH_2OH$
- Which of the following has an ester linkage?
 - (a) Nylon-6,6
- (b) Dacron
- (c) PVC
- (d) Bakelite
- **9.** If K_1 and K_2 are respective equilibrium constants for the two reactions,

(i)
$$XeF_{6(g)} + H_2O_{(g)} \Longrightarrow XeOF_{4(g)} + 2HF_{(g)}$$

$$\begin{array}{ll} \text{(i)} & \operatorname{XeF}_{6(g)} + \operatorname{H}_2\operatorname{O}_{(g)} \Longrightarrow \operatorname{XeOF}_{4(g)} + 2\operatorname{HF}_{(g)} \\ \text{(ii)} & \operatorname{XeO}_{4(g)} + \operatorname{XeF}_{6(g)} \Longrightarrow \operatorname{XeOF}_{4(g)} + \operatorname{XeO}_3\operatorname{F}_{2(g)} \end{array}$$

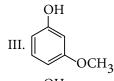
the equilibrium constant for the reaction,

 $XeO_{4(g)} + 2HF_{(g)} \Longrightarrow XeO_3F_{2(g)} + H_2O_{(g)}$

- (b) $K_1 . K_2$

- 10. XeF₆ on complete hydrolysis gives
 - (a) XeO₄
- (b) XeO₃
- (c) XeO₂
- (d) Xe
- **11.** Mark the correct order of decreasing acid strength of the following compounds.

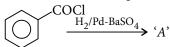








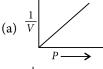
- (a) V > IV > II > I > III
- (b) II > IV > I > III > V
- (c) IV > V > III > II > I
- (d) V > IV > III > II > I
- 12. Consider the following reaction:

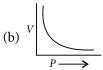


The product 'A' is

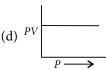
- (a) C₆H₅Cl
- (b) C₆H₅CHO
- (c) C_6H_5OH
- (d) C₆H₅COCH₃
- 13. Hinsberg's reagent is used to distinguish
 - (a) amines
- (b) alcohols
- (c) acids
- (d) amides.
- 14. The vapour pressures of ethanol and methanol are 42.0 mm Hg and 88.5 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 46.0 g of ethanol with 16.0 g of methanol. What is the mole fraction of methanol vapour?
 - (a) 0.467
- (b) 0.502
- (c) 0.513
- (d) 0.556
- **15.** Which of the following does not give a precipitate of AgCl with AgNO₃ solution?
 - (a) $[Co(NH_3)_6]Cl_3$
- (b) $[Co(NH_3)_5Cl]Cl_2$
- (c) $[Co(NH_3)_4Cl_2]Cl$ (d) $[Co(NH_3)_3Cl_3]$
- **16.** $\operatorname{Cr}_2\operatorname{O}_7^{2-} \xrightarrow{\operatorname{pH} = x} \operatorname{Cr}\operatorname{O}_4^{2-} \xrightarrow{\operatorname{pH} = y} \operatorname{Cr}_2\operatorname{O}_7^{2-}$
 - pH values *x* and *y* can be
 - (a) 4 and 5
- (b) 4 and 8
- (c) 8 and 3
- (d) 8 and 9

- **17.** Among the following oxoacids, the correct decreasing order of acid strength is
 - (a) HClO₂ > HClO₄ > HClO₃ > HOCl
 - (b) $HOCl > HClO_2 > HClO_3 > HClO_4$
 - (c) $HClO_4 > HOCl > HClO_2 > HClO_3$
 - (d) $HClO_4 > HClO_3 > HClO_2 > HOCl$
- **18.** The increasing order of the rate of HCN addition to compounds I-IV is
 - I. HCHO
- II. CH₃COCH₃
- III. PhCOCH₃(a) I < II < III < IV
- IV. PhCOPh
- (c) IV < III < II < I
- (b) IV < II < III < I
- (d) III < IV < II < I
- **19.** When first ionisation energy is plotted against the atomic number, the peaks in curve are occupied by
 - (a) halogens
- (b) rare gases
- (c) alkali metals
- (d) transition elements.
- **20.** Which is not a correct representation of Boyle's law?









- **21.** First ionisation enthalpy of Al is lower than that of Mg. This is because
 - (a) the size of Al is bigger than Mg
 - (b) ionisation enthalpy decreases in a period from left to right
 - (c) it is easier to remove electron from unpaired $3p^1$ than from paired $3s^2$
 - (d) aluminium is a passive metal while magnesium is active.
- **22.** The value of 'n' in the reaction,

$$Cr_2O_7^{2-} + 14H^+ + nFe^{2+} \longrightarrow 2Cr^{3+} + nFe^{3+} + 7H_2O$$

will be

- (a) 2
- (b) 3
- (c) 6
- (d) 7
- **23.** In Hell-Volhard-Zelinsky reaction, the carboxylic acids are halogenated at *A* position by using *B* and *C*. Identify, *A*, *B* and *C*.

A B

 \boldsymbol{C}

- (a) α NaOH Iodine
- (b) α Phosphorus Halogen
- (c) β Phosphorus H₂O
- (d) β PCl₅ NaOH

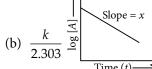
- 24. What will be the emf of the given cell? $Pt|H_2(P_1)|H_{(aq)}|H_2(P_2)|Pt$
 - (a) $\frac{RT}{F} \ln \frac{P_2}{P_1}$ (b) $\frac{RT}{2F} \ln \frac{P_1}{P_2}$ (c) $\frac{RT}{2F} \ln \frac{P_2}{P_1}$ (d) None of these
- 25. The number of atoms in 100 g of a fcc crystal with density, $d = 10 \text{ g/cm}^3$ and cell edge equal to 100 pm, is equal to
 - (a) 2×10^{25}
- (c) 4×10^{25}
- 26. At a given temperature, total vapour pressure (in torr) of a mixture of volatile components A and *B* is given by $P_{\text{total}} = 120 - 75x_B$.

The vapour pressures of pure A and B respectively (in torr) are

- (a) 120, 75
- (b) 120, 195
- (c) 120, 45
- (d) 75, 45
- **27.** The major product formed when 2-bromobutane is treated with alcoholic KOH is
 - (a) 2-butanol
- (b) 1-butene
- (c) 1-butanol
- (d) trans-2-butene.
- **28.** For a first order reaction, the graph log [A] vs t is given as follows:







- 29. The correct formula of plaster of Paris is
 - (a) $CaSO_4 \cdot 2H_2O$
- (b) CaSO₄·H₂O
- (c) $CaSiO_4 \cdot 2H_2O$ (d) $CaSO_4 \cdot \frac{1}{2}H_2O$
- **30.** ΔH_f° of water is 285.8 kJ mol⁻¹. If enthalpy of neutralisation of monoacidic strong base is -57.3 kJ mol⁻¹, ΔH_f° of OH⁻ ion will be
 - (a) $-114.25 \text{ kJ mol}^{-1}$ (b) $114.25 \text{ kJ mol}^{-1}$
 - (c) 228.5 kJ mol⁻¹
- (d) $-228.5 \text{ kJ mol}^{-1}$
- 31. A 4: 1 mixture of helium and methane is contained in a vessel at 10 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. The composition of the mixture effusing out initially is
 - (a) 8:1
- (b) 8:3
- (c) 4:1
- (d) 1:1

- 32. Four metals and their methods of refinement are given:
 - (i) Ni, Cu, Zr, Ga
 - (ii) Electrolysis, van-Arkel process, zone refining, Mond's process

Choose the right method for each.

- (a) Ni : Electrolysis, Cu : van-Arkel process, Zr : Zone refining, Ga : Mond's process
- (b) Ni: Mond's process, Cu: Electrolysis,

Zr : van-Arkel process, Ga : Zone refining

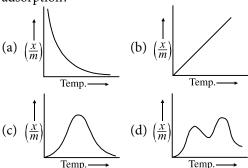
- (c) Ni : Mond's process, Cu : van-Arkel process, Zr : Zone refining, Ga : Electrolysis
- (d) Ni: Electrolysis, Cu: Zone refining, Zr: van-Arkel process, Ga: Mond's process
- 33. Haemoglobin contains 0.334% of iron by weight. The molecular weight of haemoglobin is approximately 67200 u. The number of iron atoms (Atomic weight of Fe is 56 u) present in one molecule of haemoglobin is
 - (a) 1
- (b) 2
- (c) 4
- (d) 6
- **34.** Element A forms an oxide A_2O_3 . What would be the formulae of its carbonate and phosphate?
 - (a) $A_2(CO_3)$, $A(PO_4)$ (b) $A(CO_3)$, $A_2(PO_4)_3$
 - (c) $A_2(CO_3)_3$, $A(PO_4)$ (d) $A_2(CO_3)_3$, $A_2(PO_4)_3$
- 35. The two functional groups present in a typical carbohydrate are
 - (a) -OH and -COOH
 - (b) -CHO and -COOH
 - (c) $\geq C = O$ and -OH
 - (d) -COOH and -CHO
- **36.** The total number of possible isomers of the complex compound [Cu^{II}(NH₃)₄][Pt^{II}Cl₄] is
 - (a) 3
- (b) 6
- (c) 5
- (d) 4
- 37. 2-Phenylethanol may be prepared by the reaction of phenyl magnesium bromide with
 - (a) HCHO
- (b) CH₃CHO
- (c) CH₃COCH₃
- **38.** $C_8H_{10}(A)$ oxidative cleavage by $C_3H_5COOH(B)$. Thus, A and B respectively are
 - (a) $CH_2=CHCH_2C=CCH_2CH=CH_2$, CH2=CHCH2COOH
 - (b) \rightarrow C \equiv C \rightarrow , \rightarrow COOH
 - (c) both (a) and (b) are correct
 - (d) none of the above is correct.

39. In which of the following orbital diagrams are both Pauli's exclusion principle and Hund's rule violated?





- 40. Which one of the following acts as an oxidising agent?
 - (a) Tb⁴⁺
- (b) Sm²⁺
- (c) Eu²⁺
- (d) Yb^{2+}
- 41. Nitrogen in an organic compound can be estimated
 - (a) Kjeldahl's method
 - (b) Carius method
 - (c) Victor Meyer's method
 - (d) Lassaigne's method.
- **42.** The maximum kinetic energy of the photoelectrons is found to be 6.63×10^{-19} J. When the metal is irradiated with a radiation of frequency 2×10^{15} Hz, the threshold frequency of the metal is about
 - (a) $2 \times 10^{15} \,\mathrm{s}^{-1}$
- (b) $1 \times 10^{15} \,\mathrm{s}^{-1}$
- (c) $2.5 \times 10^{15} \,\mathrm{s}^{-1}$
- (d) $4 \times 10^{15} \,\mathrm{s}^{-1}$
- 43. Which of the following represents physical adsorption?



- 44. The number of possible resonance structures for CO_3^{2-} is
 - (a) 2
- (b) 3
- (c) 6
- (d) 9
- 45. Amount of oxalic acid present in a solution can be determined by its titration with KMnO₄ solution in the presence of H₂SO₄. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl
 - (a) oxidises oxalic acid to carbon dioxide and
 - (b) gets oxidised by oxalic acid to chlorine

- (c) furnishes H⁺ ions in addition to those from oxalic acid
- (d) reduces permanganate to Mn²⁺.
- **46.** Which of the following is incorrect with respect to Frenkel defect?
 - (a) One or more ions (generally cations) shift from lattice points to interstitial sites.
 - (b) It appears in ionic compounds having high coordination number.
 - (c) r^+/r^- ratio should be low.
 - (d) All of the above.
- **47.** H₂O₂ is manufactured these days by
 - (a) electrolysis of 50% H₂SO₄
 - (b) the action of H₂SO₄ on Na₂O₂
 - (c) the action of H_2O_2 on BaO_2
 - (d) burning hydrogen in excess of oxygen.
- 48. 17.675 is rounded off to four significant figures as
 - (a) 17.68
- (b) 17.67
- (c) 17.6750
- (d) 17.7
- 49. Ge(II) compounds are powerful reducing agents whereas Pb(IV) compounds are strong oxidants. This can be due to
 - (a) Pb is more electropositive than Ge
 - (b) ionization potential of Pb is less than that of
 - (c) ionic radii of Pb²⁺ and Pb⁴⁺ are larger than those of Ge²⁺ and Ge⁴⁺
 - (d) more pronounced inert pair effect in Pb than in Ge.
- **50.** Rutherford's experiment which established the nuclear model of the atom used a beam of
 - (a) β-particles which impinged on a metal foil and got absorbed
 - (b) γ-rays which impinged on a metal foil and ejected electrons
 - (c) helium atoms, which impinged on a metal foil and got scattered
 - (d) helium nuclei, which impinged on a metal foil and got scattered.
- **51.** E_1 , E_2 and E_3 are the emf values of the three given Galvanic cells respectively.
 - (i) $Zn|Zn^{2+}(1 M)||Cu^{2+}(0.1 M)|Cu$

 - (ii) $Zn|Zn^{2+}(1 M)||Cu^{2+}(1 M)|Cu$ (iii) $Zn|Zn^{2+}(0.1 M)||Cu^{2+}(1 M)|Cu$
 - Which one of the following is true?
 - (a) $E_2 > E_3 > E_1$
- (b) $E_3 > E_2 > E_1$
- (a) $E_2 > E_3 > E_1$ (b) $E_3 > E_2 > E_1$ (c) $E_1 > E_2 > E_3$ (d) $E_1 > E_3 > E_2$

- 52. To prepare an ether by Williamson's synthesis, the reactants needed are
 - (a) ethyl alcohol and tert-butyl alcohol
 - (b) sodium ethoxide and tert-butyl bromide
 - (c) sodium tert-butoxide and ethyl bromide
 - (d) sodium ethoxide and sodium tert-butoxide
- 53. The correct order of acidic nature of oxides is in the
 - (a) $NO < N_2O < N_2O_3 < NO_2 < N_2O_5$
 - (b) $N_2O < NO < N_2O_3 < NO_2 < N_2O_5$
 - (c) $N_2O_5 < NO_2 < N_2O_3 < NO < N_2O$
 - (d) $N_2O_5 < N_2O_3 < NO_2 < NO < N_2O$.
- **54.** Compound *X* is highly volatile and insoluble in water. Bonding in *X* is
 - (a) ionic
- (b) covalent
- (c) polar covalent
- (d) coordinate.
- 55. At a particular temperature under high pressure $K_{w}(H_{2}O) = 1 \times 10^{-10}$.

A solution of pH 5.4 under these conditions is said to be

- (a) acidic
- (b) basic
- (c) neutral
- (d) amphoteric.
- **56.** In coagulating the colloidal solution of As₂S₃ which of the following has the minimum coagulating value?
 - (a) NaCl
- (b) KCl
- (c) BaCl₂
- (d) AlCl₃
- **57.** In an irreversible process taking place at constant Tand P and in which only pressure-volume work is being done, the change in Gibbs' free energy (dG)and change in entropy (dS) satisfy the criteria
 - (a) $(dS)_{V, E} < 0, (dG)_{TP} < 0$
 - (b) (dS) > 0, $(dG)_{TP} < 0$
 - (c) (dS) = 0, $(dG)_{TP} = 0$
 - (d) $(dS) = 0, (dG)_{TP} > 0$
- **58.** Which of the following statements photochemical smog is incorrect?
 - (a) It is also called as Los Angeles smog.
 - (b) It has low concentration of oxidising agents.
 - (c) It can be controlled by controlling the release of NO₂, hydrocarbons, etc.
 - (d) Plantation of some plants like pinus helps in controlling photochemical smog.
- **59.** Major product of the following S_N1 reaction is

$$\begin{array}{ccc} \operatorname{CH_3CHCHCH_3} + \bar{\operatorname{OC}}_2\operatorname{H}_5 & \longrightarrow \\ & | & | & \\ & \operatorname{Br} & \operatorname{CH}_3 & \end{array}$$

- (c) CH₃CH₂CCH₃ (d) none is correct. OC₂H₅
- **60.** Aniline on treatment with HCl and NaNO₂ at low temperature gives
 - (a) aminophenol
- (b) chloroaniline
- (c) diazonium salt
- (d) nitroaniline.

SOLUTIONS

1. (a)

O CH₃

$$2 \parallel 3 \parallel 4$$

2. (a): CH₃-C-CH-CH₃
3-Methylbutan-2-one

- (d): Saccharin is 550 times sweeter than sucrose, 3. aspartame is 100 times sweeter than sucrose. Sucralose is 600 times sweeter than sucrose.
- **4.** (a): Branching decreases the boiling point.
- 5. (a): For the reaction, $2A + B \rightarrow C + D$ Rate of reaction

$$= -\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

Now, rate of reaction, $\frac{d[C]}{dt} = k[A]^x[B]^y$ From table,

$$1.2 \times 10^{-3} = k(0.1)^x (0.1)^y$$
 ...(i)

$$1.2 \times 10^{-3} = k(0.1)^{x} (0.2)^{y}$$
 ...(ii)

$$2.4 \times 10^{-3} = k(0.2)^{x} (0.1)^{y}$$
 ...(iii)

On dividing equation (i) by (ii), we get

$$\frac{1.2 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k(0.1)^x (0.1)^y}{k(0.1)^x (0.2)^y}$$

$$1 = \left(\frac{1}{2}\right)^y \implies y = 0$$

On dividing equation (i) by (iii), we get

$$\frac{1.2 \times 10^{-3}}{2.4 \times 10^{-3}} = \frac{k(0.1)^x (0.1)^y}{k(0.2)^x (0.1)^y}$$

$$\left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^x \implies x = 1$$

Hence,
$$\frac{d[C]}{dt} = k[A]^{1}[B]^{0} = k[A]$$

7. (d):
$$NH_2$$
 $N_2^+Cl^ N_2^+Cl^ N$

$$CN$$
 H_2/Ni
 $(Reduction)$
 CH_2NH_2
 CH_2NH_2
 CH_2NH_2
 CH_2NH_2
 CH_2NH_2
 CH_2NH_2
 CH_2NH_2

8. (b): When a diacid is condensed with dialcohol, the polymer obtained contains ester linkage.

$$n \text{HOCH}_2\text{CH}_2\text{OH} + n \text{HOOC} \longrightarrow \text{COOH}$$
Ethylene glycol (dialcohol)
$$(\text{dialcohol}) \qquad \text{Terephthalic acid} \qquad \text{(diacid)} \qquad \text{(diacid)} \qquad \text{(diacid)} \qquad \text{(diacid)} \qquad \text{(diacid)} \qquad \text{(Diacron)}$$

- **9. (d):** Reaction (ii) and reverse of reaction (i) gives the desired reaction hence, $K = K_2 \times \frac{1}{K_1} = \frac{K_2}{K_1}$.
- 10. (b): XeF₆ on complete hydrolysis yields xenon trioxide, XeO₃.
 XeF₆ + 3H₂O → XeO₃ + 6HF
- 11. (b): Phenols are acidic in nature due to resonance stabilisation of phenoxide ion. Presence of electron withdrawing groups (such as —NO₂, —X, NR₃, —CHO, —COX, —COOR, —CN) in the ring stabilises phenoxide ion and increases the acidic nature of phenols. On the other hand, presence of electron releasing groups (such as —CH₃, —OR) in the ring destabilises the phenoxide ion and decreases the acidic nature of phenols.

Furthermore, *meta*-isomer of nitrophenol is less acidic than *p*-and *o*-isomers because it is stabilised by inductive effect only. Similarly, *meta*-isomer of methoxyphenol is destabilised to lesser extent than the *para*-isomer.

Thus, correct order of acidic strength is II > IV > I > III > V.

12. (b):
$$C-Cl \xrightarrow{H_2/Pd-BaSO_4/S} C-H$$

It is Rosenmund reduction.

- **13.** (a): Hinsberg's reagent (C₆H₅SO₂Cl) is used to distinguish amines.
- 14. (c):
 $CH_3OH(A)$ $C_2H_5OH(B)$

 Vapour pressure
 88.5 mm Hg
 42.0 mm Hg

 Mass
 16.0 g
 46.0 g

 No. of moles
 0.5
 1

:. Total moles = 1 + 0.5 = 1.5

$$P_{\text{total}} = p_A^{\circ} x_A + p_B^{\circ} x_B = \frac{88.5 \times 0.5}{1.5} + \frac{42 \times 1}{1.5}$$

 $P_{\text{total}} = 29.5 + 28 = 57.5 \text{ mm Hg}$

Mole fraction of methanol in vapour phase is y_A .

$$p_A = y_A \times \text{Total pressure}$$
$$y_A = \frac{29.5}{57.5} = 0.513$$

- **15.** (d): [Co(NH₃)₃Cl₃] does not ionise to furnish Cl⁻ ion as no chlorine atom is present outside the coordination sphere. Evidently, it would not give white precipitate with AgNO₃.
- 16. (c): $Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O;$ pH > 7 (x > 7) $2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O;$ pH < 7 (y < 7)
- 17. (d): No. of O-atoms (i.e. oxidation state)

 Acidic strength Hence, the decreasing order of acidic strength will be HClO₄ > HClO₃ > HClO₂ > HOCl
- **18. (c)**: Addition of HCN is a nucleophilic addition reaction. Greater the electron deficiency of carbonyl group, higher is the rate of reaction. Hence,

19. (b): Generally, the first ionization energy increases as we go across a period. Hence, the maximum peaks in curve are occupied by rare gases.

- **21.** (c): Electronic configuration of Al $1s^2 2s^2 2p^6 3s^2 3p^1$ Electronic configuration of Mg - $1s^22s^22p^63s^2$ It is difficult to remove electron from paired $3s^2$ -orbital than the unpaired $3p^1$. Hence, *I.E.*₁ of Al is lower than Mg.
- 22. (c): $Cr_2O_7^{2-} + 14H^+ + nFe^{2+} \longrightarrow 2Cr^{3+} + nFe^{3+} + 7H_2O$ $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ (reduction) ...(i)

$$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$$
 (oxidation) ...(ii)

Eq. (ii) is multiplied by 6,

$$6\text{Fe}^{2+} \longrightarrow 6\text{Fe}^{3+} + 6e^{-1}$$

Thus, balanced equation is

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

Hence, the value of n is 6.

- 23. (b): $RCH_2COOH \xrightarrow{(i) X_2/P} R-CH-COOH$
- **24. (b)**: Anode: $H_2(P_1) \longrightarrow 2H^+ + 2e^-$ Cathode: $2H^+ + 2e^- \longrightarrow H_2(P_2)$ $H_2(P_1) \longrightarrow H_2(P_2)$

$$E_{\rm cell} = E^{\circ}_{\rm cell} - \frac{RT}{nF} \ln \frac{P_2}{P_1} = \frac{RT}{2F} \ln \frac{P_1}{P_2}$$

25. (c): Mass (m) = 100 g; Density (d) = 10 g/cm³ and length (l) = 100 pm = 100 × 10⁻¹² m = 100 × 10⁻¹⁰ cm We know that volume of the unit cell = $(a)^3$ = $(100 \times 10^{-10} \text{ cm})^3$ = 10^{-24}cm^3

and volume of 100 g of element

$$=\frac{Mass}{Density} = \frac{100}{10} = 10 \text{ cm}^3$$

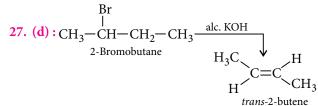
Therefore, number of unit cells = $\frac{10}{10^{-24}} = 10^{25}$

Since each fcc cube contains 4 atoms, therefore total number of atoms in 100 g = 4×10^{25} .

26. (c): $P_{\text{total}} = p_A^{\circ} x_A + p_B^{\circ} x_B$ $= p_A^{\circ}(1 - x_B) + p_B^{\circ}x_B = p_A^{\circ} - (p_A^{\circ} - p_B^{\circ})x_B$ $= 120 - 75x_B$ (given)

Thus, $p_A^{\circ} = 120 \text{ torr}$

$$p_A^{\circ} - p_B^{\circ} = 75 \text{ torr}, \quad \therefore \quad p_B^{\circ} = 45 \text{ torr}$$



28. (c): For first order reaction,

$$\log[A] = -\frac{kt}{2.303} + \log[A]_0$$

$$Slope = -\frac{k}{2.303}$$

- 29. (d): Plaster of Paris is calcium sulphate hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$.
- **30.** (d): $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2 O_{(l)}; \Delta H_f^{\circ} = -285.8 \text{ kJ mol}^{-1}$

$$H_{(aq)}^+ + OH_{(aq)}^- \longrightarrow H_2O_{(l)}; \Delta H_{neut}^o = -57.3 \text{ kJ mol}^{-1}$$

$$\frac{1}{2} \operatorname{H}_{2(g)} \longrightarrow \operatorname{H}^{+}_{(aq)} + e^{-}; \Delta H^{\circ}_{f} = 0 \text{ (by convention)}$$
...(iii)

$$\frac{1}{2} \text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} + e^{-} \longrightarrow \text{OH}_{(aq)}^{-}$$

$$\Delta H_{f}^{\circ} \text{ of OH}^{-} = -285.8 + 57.3 = -228.5 \text{ kJ mol}^{-1}$$

31. (a): Pressure of helium = 8 bar, $CH_4 = 2$ bar According to Graham's law,

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

$$\frac{r_{\text{He}}}{r_{\text{CH}_4}} = \frac{P_{\text{He}}}{P_{\text{CH}_4}} \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} = \frac{8}{2} \sqrt{\frac{16}{4}} = \frac{8}{1} = 8:1$$

32. (b): Ni — Mond's process;

Cu — Electrolysis;

Zr — van-Arkel process;

Ga — Zone refining

33. (c): : 100 g of haemoglobin contains = 0.334 g Fe

67200 g of haemoglobin contains

$$= \frac{0.334 \times 67200}{100} = 224.45 \text{ g Fe}$$

Now,

 \therefore 56 g iron = 1 mole of Fe atoms

$$\therefore 224.45 \text{ g iron} = \frac{1 \times 224.45}{56}$$
$$= 4 \text{ moles of Fe atoms}$$

- ∴ 1 molecule of haemoglobin = 4 Fe atoms
- **34.** (c): $A_2O_3 \Rightarrow \text{Valency of } A \text{ is 3.}$ So, the formulae of carbonate (CO_3^{2-}) will be $A_2(CO_3)_3$ and that of phosphate (PO_4^{3-}) will be $A(PO_4)$.
- **35.** (c): Carbohydrates are essentially polyhydroxy aldehydes and polyhydroxy ketones. Thus, the two functional groups present are >C = O (aldehyde or ketone) and −OH.
- **36.** (d): For $[Cu^{II}(NH_3)_4][Pt^{II}Cl_4]$, four isomers are possible which are $[Cu(NH_3)_4][PtCl_4]$, $[CuCl_4][Pt(NH_3)_4]$, $[PtCl_3(NH_3)][Cu(NH_3)_3Cl]$ and $[Pt(NH_3)_3Cl][Cu(NH_3)Cl_3]$.

37. (d): C₆H₅MgBr + O Ether

Phenyl magnesium
bromide

C₆H₅CH₂CH₂OMgBr
$$\xrightarrow{H^+/H_2O}$$

C₆H₅CH₂CH₂OHgBr

2-Phenylethanol

Oxidative cleavage

COOH

Formation of *B* indicates that *A* is symmetrical.

- **39.** (d): Two electrons with parallel spins in the same orbital are violating Pauli's exclusion principle whereas pairing without single occupancy of all orbitals is violating Hund's rule.
- **40.** (a): All those inner-transition elements having +2 oxidation state, change to +3, and act as reducing agents. While those having +4 oxidation state tend to change to +3 oxidation state and act as oxidising agents. Therefore, Tb⁴⁺ acts as an oxidising agent.
- **41. (a)**: Nitrogen can be estimated by Kjeldahl's method. This method cannot be used for organic compounds (i) containing nitrogen in the ring. *e.g.*, pyridine, quinoline etc. (ii) containing nitro and diazo groups. However, Lassaigne's test is used to detect nitrogen.

42. (b): Kinetic energy =
$$h(v - v_0)$$

 $KE = hv - hv_0$
 $v_0 = v - \frac{KE}{h} = 2 \times 10^{15} - \frac{6.63 \times 10^{-19}}{6.63 \times 10^{-34}}$
 $= 1 \times 10^{15} \text{ s}^{-1}$

43. (a): The amount of adsorption decreases with rise in temperature in case of physical adsorption.

44. (b):
$$\overset{.\dot{O}}{:}$$
 $\overset{.\dot{O}}{:}$ $\overset{.\dot{O}}{:}$

45. (d): Oxalic acid present in a solution can be determined by its titration with KMnO₄ solution in the presence of H₂SO₄.

$$2KMnO_4 + 3H_2SO_4 + 5 \mid COOH \longrightarrow COOH$$

$$K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O_3$$

Titration cannot be done in the presence of HCl because $KMnO_4$ being a strong oxidising agent oxidises HCl to Cl_2 and itself gets reduced to Mn^{2+} . So, actual amount of oxalic acid in solution cannot be determined.

- **46. (b):** Frenkel defect appears in ionic crystals having low coordination number, *i.e.*, low r^+/r^- ratio. The void can accommodate small cation easily.
- **47.** (a): H₂O₂ is manufactured by electrolysis of 50% sulphuric acid.
- 48. (a)

C₃H₅COOH

- **49.** (d): Ge⁴⁺ is more stable than Ge²⁺ as a result of which Ge²⁺ has a tendency to be oxidised to Ge⁴⁺ so, Ge²⁺ compounds act as powerful reducing agents. But Pb²⁺ is more stable than Pb⁴⁺ because of pronounced inert pair effect as a result of which Pb⁴⁺ has a tendency to get reduced to Pb²⁺ so, Pb⁴⁺ compounds act as strong oxidising agents (*i.e.*, oxidants).
- **50.** (d): Rutherford used doubly charged helium particles (α -particles).

51. (b):
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Higher the $\frac{[Zn^{2+}]}{[Cu^{2+}]}$ ratio lower is the emf of cell.

(i)
$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = 10;$$
 (ii) $\frac{[Zn^{2+}]}{[Cu^{2+}]} = 1$

(iii)
$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = 0.1$$

So, order is $E_3 > E_2 > E_1$.

52. (c): 1° alkyl halides on treatment with an alkoxide ion tend to undergo substitution to form ethers. So, sodium *tert*-butoxide and ethyl bromide reagent is used.

53. (b): The acidic character of oxides increases with increase in oxidation number of element. However,

- **54. (b)**: Compounds which are insoluble in water have covalent bonds. Due to their low boiling points, they are highly volatile.
- **55. (b)**: $K_w = 1 \times 10^{-10}$ \therefore [H⁺] = [OH]⁻ = 10⁻⁵ M Thus, pH = 5 for neutral solution. pH < 5 acidic, pH > 5 basic
- **56.** (d): As_2S_3 is a negative sol. For coagulating negative sol, Al³⁺ is most effective. Higher the magnitude of the charge, lower is the coagulating value.
- 57. (b): An irreversible process is spontaneous hence, entropy increases and free energy decreases.
- 58. (b): Photochemical smog has high concentration of oxidising agents and it can be controlled by controlling the release of NO2, hydrocarbons, etc. Plantation of some plants like pinus helps in controlling photochemical smog.

59. (c):
$$CH_3CHCHCH_3 \xrightarrow{S_N 1} CH_3^+CHCHCH_3$$

Br CH_3
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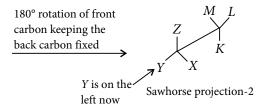
ADVANCED CHEMISTRY BLOC

(SAWHORSE AND NEWMAN PROJECTIONS)

Mukul C. Ray, Odisha

SAWHORSE AND NEWMAN PROJECTIONS

Sawhorse projection is used to show relative spatial arrangement (arrangement in space) of atoms or groups attached to two adjacent carbons (not necessarily chiral). The backbone carbons are represented by a diagonal line and the terminal carbons are shown in groups. The top carbon of Fischer projection becomes the back carbon group of Sawhorse projection.

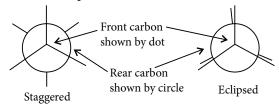


Note that in Sawhorse projection-1, while the Z and K groups are facing downward, L and Y are on the right and X and M are on the left as were in the Fischer projection. Whereas in Sawhorse projection-2, Z is facing upward (while K remains as it was), X is on the right and Y is on the left. This format is always true and can be used as a tip to convert Fischer to Sawhorse.

Free clockwise or anticlockwise rotation of one carbon keeping the other fixed is permissible in a Sawhorse projection, also called as 'Perspective Formula'.

The steric interaction between atoms or groups in three-dimensional space is nicely visualized by Newman projection formula. The central dot represents the first carbon and the 'circle' stands for the back carbon. Lines projected from the dot and the perimeter of the circle carry the atoms or groups attached to the respective carbons.

Newman projection formula in which the atoms or groups attached to two carbons, one shown by dot and the other by a circle, lie in a straight line is called the 'eclipsed form'. Atoms or groups attached to front carbon obscure or hide those attached to the rear (or back) carbon, hence the title. The other form of Newman projection though is generally called as 'staggered' but sometimes called as 'gauche' or 'skew' depending upon the nature and position of the substituents.



While converting a Sawhorse projection formula to a Newman form, simply the front and the rear carbons are copied along with their substituents.

$$Z = X \times X$$

$$X \times X$$
Sawhorse projection
$$X \times X \times X$$
Newman projection

Note that unlike Fisher projection formula, the carbons demonstrated in Sawhorse or Newman projection formulae are not necessarily chiral carbons.

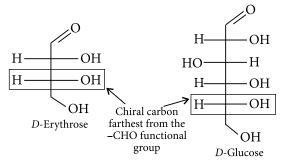
Problem-1: Write Fischer projection formulae for the following compounds.

(a)
$$H_2N$$
 H CH_3 (b) H CH_3 CH_3

RELATIVE AND ABSOLUTE NAMING

Naming the stereoisomers using prefixes cis, trans, syn, anti, D (not to be confused with d used for dextrorotatory substance) and L (not to be confused with l used for laevorotatory substance) is an attempt to show the relative configuration. For example, in cis-but-2-ene, $-CH_3$ attached to one carbon is cis or on the same side as the $-CH_3$ attached to the other carbon of the double bond. This is what is known as 'relative configuration'.

Without taking the spatial arrangement of groups around both the carbons simultaneously a stereoisomer cannot be called as *cis* or *trans*. Similar is the way for assigning *D* and *L* configuration for sugar molecules. The compound relative to which the configurations of sugars are described is the glyceraldehyde. It is taken as an arbitrarily standard. Glyceraldehyde molecule with –H on the left is given as 'D'. Any other aldose sugar molecules having –H on the left at the chiral carbon farthest from the –CHO functional group is termed as 'D'.

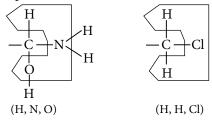


The idea though can be extended to other chiral centers but has a number of limitations. To overpower these difficulties, absolute system of naming stereocentres have been developed. In this method, one stereocentre can be directly named without comparing it with another stereocentre. The method is known as 'absolute configuration'.

THE SEQUENCE RULE

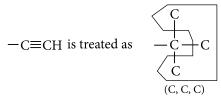
Consider the following rules without naming them as rule-1, 2 ... etc.

- The higher the atomic number of the immediate substituent atom, the higher is the priority. For example, -H < -C < -N < -O < -Cl.
- For different isotopes, the heavier isotope takes precedence.
 For example, -D > -H
- If the immediate substituent atoms are same, move to the next set of three atoms. The set with at least one atom having higher atomic number takes precedence.



Since (H, H, Cl = 1, 1, 17) takes superiority over (H, N, O = 1, 7, 8), $-CH_2Cl$ gets the higher priority as compared to $-CH(OH)NH_2$.

• If a double or triple bond is attached to the substituent atom under consideration, the set of three atoms is picked as shown below.



A doubly bonded atom attached to substituent is considered twice and a triply bonded atom is considered thrice to get the set of three atoms and then the previous priority rule is then applied to decide the precedence. The set (C, C, C = 6, 6, 6) takes preference over the set (H, C, C = 1, 6, 6). Thus, $-C \equiv CH$ takes priority over $-CH \equiv CH_2$. Consider another example,

The set (O, O, O = 8, 8, 8) takes priority over the set (O, O, H = 8, 8, 1). As a result, -COOH gets higher priority as compared to -CHO.

R/S SYSTEM OF NOMENCLATURE (CAHN-INGOLD-PRELOG OR CIP SYSTEM)

Look at the following stereocentre:

CIP system is used to describe the configuration of the stereocentre directly without comparing it with any other stereocentre whose configuration is arbitrarily assigned (like glyceraldehyde). Follow the simple steps.

• Following the sequence rules, allot priority order to the substituents attached to the stereocentre.

• Hold the model in such a way so that the atom having lowest priority (H here) remains at farthest distance from your eyes.

O Draw an arrow mark in a circular way starting from atom of highest priority (iodine) to the third most priority (chlorine) *via* the second most (bromine) means.

Front view

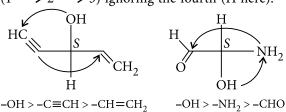


• If the arrow mark moves in a clockwise manner, the configuration assigned is 'R' and if in the anticlockwise manner, the configuration assigned is 'S'. The alphabet 'R' stands for 'rectus' or right and 'S' stands for 'sinister' means left.



The method is most widely used on Fischer projections. So, here are the rules to assign the configurations of stereocentres in Fischer projection formulae.

O Assign priorities to the substituents attached to the stereocentre and then check whether the substituent with lowest priority is on the vertical line or not. If yes, draw the arrow mark starting from the top most priority to the third most *via* the second most (1 → 2 → 3) ignoring the fourth (H here).



If the atom with lowest priority is on the horizontal line, rotate the Fischer projection in such a way so that the atom or group with lowest priority is brought to the vertical line. While rotating the Fischer projection formula on the plane of the paper, the restrictions must be kept in mind.

OH Rotate the three in clockwise fashion keeping the OH fixed

$$H_2N$$
 H
 Cl
 H
 C

Consider some more examples where more than one chiral carbon centers are there. In such cases, each individual center has to be checked separately.

$$\begin{array}{c|c} H \\ H_3C & \begin{array}{c|c} I \\ \hline R \\ \hline \end{array} \\ H_3C & \begin{array}{c|c} I \\ \hline R \\ \hline \end{array} \\ CH(Cl)CH_3 \\ \hline \\ CH_3 & \begin{array}{c|c} CH(Br)CH_3 \\ \hline \\ CH_3 \\ CH_3 \\ \hline \\ CH_3 \\ CH_3 \\ \hline \\ CH_3 \\ CH_3 \\ \hline \\ CH_3 \\ CH_3 \\ \hline \\ CH_3 \\ \hline \\ CH_3 \\ CH_3 \\ \hline \\ CH_3 \\ CH_4 \\ CH_3 \\ CH_5 $

In case the chiral center is a part of ring system, it can be proceeded as follows:

The configuration of chiral center is 'S' here. –OH group takes the highest priority. In order to decide the next, we move along the ring both in upward and in downward directions. In the first point, we come

across $-CH_2$ - units in both the ways. Then comes the real difference, one -CO- group and another $-CH_2$ - unit. -H gets the lowest priority. Priority order of the substituents then has been shown in circles as 1, 2, 3 and 4 (A) and the ring dropped for the sake of simplicity, then rotated the structure like a steering wheel towards right (B) and then have converted it into the proper Fischer projection formula (C).

one
$$-CH_2$$
-centre

H
Carbon carrying doubly bonded oxygen

Another $-CH_2$ - centre

Another $-CH_2$ - centre

Another $-CH_2$ - centre

Another $-CH_2$ - centre

The following steps are as usual to bring the lowest substituent to the vertical line and then to check the configuration.

$$0 \longrightarrow 3 \longrightarrow 3 \longrightarrow 3$$

TIPS TO HANDLE R/S SYSTEM OF NOMENCLATURE

The following tips can help only in the final step; though small but it is extremely handy. When the substituent with the lowest priority remains in the horizontal line, normally rotate the Fischer projection in such a way so as to bring it to the vertical line. Then assign 'R' or 'S' to the chiral center. To recall it take another example.

Instead of bringing the fourth priority to the vertical line, if the configuration is assigned directly, the result will be wrong, wrong but exactly opposite of the correct answer.

Br
$$R$$
 H is on the horizontal line (wrong answer)

Without bringing the group with lowest priority to the vertical line, it can be done directly. The tips are:

- When the group with lowest priority is on the vertical line, check the direction of arrow mark from 1 to 2 to 3 and assign the configuration.
- When the group with lowest priority is on the horizontal line, check the direction of arrow mark from 1 to 2 to 3 and find out the configuration. If it is 'R', then correct answer is 'S' and vice-versa.

Problem-2: Assign 'R' and 'S' notation to the chiral centers in the following compounds.

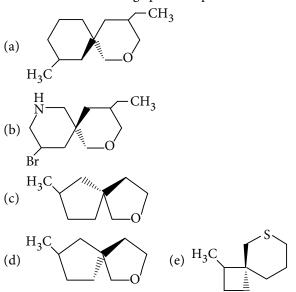
Problem-3: Assign '*R*' and '*S*' notation to the chiral centers in the following compounds.

Problem-4: Assign '*R*' and '*S*' notation to the chiral centers of the following ring compounds.

$$(a) \overset{H}{\overset{\dot{\mathbb{H}}}{\longrightarrow}} NH_2 \qquad (b) \overset{CH_3}{\overset{\dot{\mathbb{H}}}{\longrightarrow}} OH$$

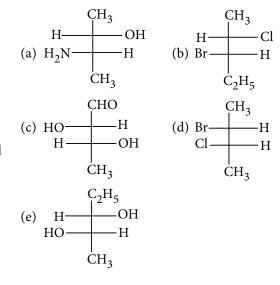
Br
$$CH_3$$
 (d) H_0 H_3 H_3 H_4 H_4 H_4 H_5 H_5 H_4 H_5 H_5 H_6 H_6 H_6 H_7 H_8 H_8

Problem-5: Assign '*R*' and '*S*' notation to the chiral centers of the following spiro compounds.



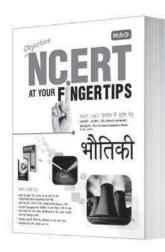
SOLUTIONS

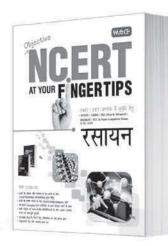
Problem-1:

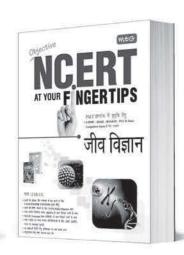


PMT/PET के Entrance Exam में हिंदी माध्यम छात्रों के लिए Triple धमाका

NCERT Textbook पर Based भौतिकी, रसायन और जीव विज्ञान की Objective पुस्तकें







NCERT पाठ्यक्रम पर आधारित और हमारे Subject Experts द्वारा निर्मित 10,000 से अधिक Objective Type प्रश्नों का अभ्यास कर इन तीनों विषयों पर अपनी महारत हासिल कर परीक्षाओं में अधिकतम सफलता प्राप्त करें और विजयी बनें।

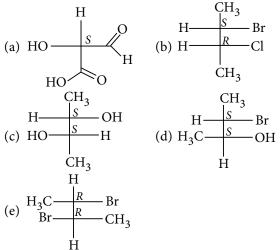
ये तीनों पुस्तकें ही क्यों पढ़नी जरूरी हैं?

- प्रश्नों को शीघ्रता और सरलता से हल करने के लिए CHAPTERWISE SYNOPSIS (मुख्य बिंदू)
- छात्रों की प्रगति जाँचने के लिए TOPICWISE Objective प्रश्न
- NCERT Exemplar (प्रश्न प्रदर्शिका) के प्रश्न विस्तृत उत्तरों के साथ
- सभी राष्ट्रीय एवं राज्य स्तरीय प्रतियोगिताओं के लिए अत्यंत उपयोगी, सरल एवं महत्त्वपूर्ण पुस्तकें
- AIIMS | JEE की तैयारी हेतू अभिकथन एवं तर्क प्रारूप प्रश्न
- स्वमूल्यांकन हेतु पाँच अभ्यास प्रश्न पत्र



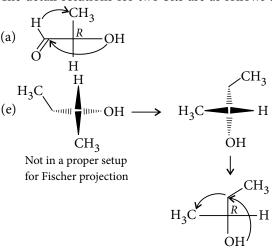
MTG Learning Media (P) Ltd. Plot #99, Sector 44, Gurgaon - 122 003 (HR) ये पुस्तकें देश के सभी शीष पुस्तक विक्रेताओं के पास उपलब्ध हैं। अधिक जानकारी हेतु कृप्या संपर्क करें: 0124-6601200 or e-mail:info@mtg.in

Problem-2:



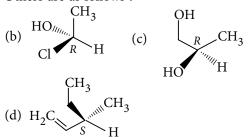
Problem-3:

The detail solutions for two bits are as follows:



Since H is in the horizontal line anti-clockwise arrow gives *R*

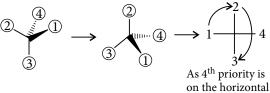
Others are as follows:



Problem-4:

70 CHEMISTRY TODAY | MAY '16

After priority assignment and ignoring the ring, the molecule will look like

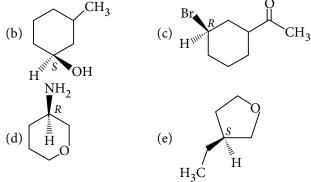


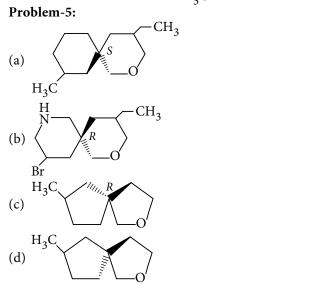
on the horizontal line, it is S

CH₃

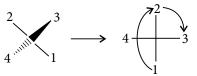
Br
R

O

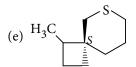




After assigning priority and ignoring the rings, it would look like



Since 4^{th} priority is on the horizontal line, it is S





CHEMISTRY MUSING

SOLUTION SET 33

1. (a): In octahedral complexes,

$$d^{8} \quad \boxed{1 | 1 | 1 |} \quad \boxed{\uparrow} \uparrow$$

 $CFSE_{Octahedral} = -0.4n_x + 0.6n_y$

 $(n_x = \text{no. of electrons in } t_{2g} \text{ and } n_y = \text{no. of electrons}$

 $CFSE_{octahedral} = -0.4(6) + 0.6(2) = -1.2 \Delta_o$ In tetrahedral complexes,

 $\begin{array}{ccc}
e_g & t_{2g} \\
\hline
11 & 11
\end{array}$ $CFSE_{tetrahedral} = -0.6n_x + 0.4n_v$ $= -0.6(4) + 0.4(4) = -0.8 \Delta_t$

Now, $\Delta_t = \frac{4}{9} \Delta_o$

 \therefore CFSE_{tetrahedral} = $-0.8 \left(\frac{4}{9} \Delta_o \right) = -0.36 \Delta_o$

2. (c): In S_N1 reactions, formation of carbocation is the rate determining step. Hence, the alkyl halide which forms most stable carbocation intermediate will show highest reactivity.

In option (c), the benzylic carbocation formed is most stable due to resonance thus, it is most reactive.

3. (a): $R-C-Cl + R'NH_2 \longrightarrow R-C-NHR' + HCl$ HCl formed in this reaction protonates unreacted amine and since protonated amines are not nucleophiles, the further reaction with acyl chloride stops.

$$R'NH_2 + HCl \longrightarrow RNH_3 + Cl$$
No nucleophilic site

$$R - C - Cl + RNH_3 \longrightarrow$$
 no reaction

Hence, reaction must be carried out with twice as much amine as the acyl chloride.

$$\begin{array}{c|c}
O & O \\
\parallel & \parallel \\
R - C - Cl + R' - OH \xrightarrow{\text{Pyridine}} R - C - OR' + HCl \\
\text{Acyl chloride} & \text{Ester}
\end{array}$$

Reaction with acid chloride is carried out in presence of pyridine (base) to neutralise HCl formed during the reaction. It shifts the equilibrium towards right hand side.

4. (c): Let r_1 , r_2 , $-r_3$ be the rotation per mole of sucrose, glucose and fructose respectively.

Sucrose → Glucose + Fructose

at
$$t = 0$$
 a 0 0 at time t $a - x$ x x

$$ar_1 = 32.4 \implies a = \frac{32.4}{85} = 0.38$$

$$(a - x)r_1 + xr_2 - xr_3 = 28.8$$

$$x(r_2 - r_3 - r_1) = 28.8 - 32.4 = -3.6$$

$$x(74 - 86.04 - 85) = -3.6 \implies x = 0.037$$

For a first order reaction,

$$k = \frac{2.303}{t} \log \left(\frac{a}{a - x} \right)$$

$$k = \frac{2.303}{10} \log \left(\frac{0.38}{0.38 - 0.037} \right)$$

$$k = 9.21 \times 10^{-3} \,\mathrm{min}^{-1}$$

$$\therefore t_{1/2} = \frac{0.693}{k} = 75.2 \text{ min}$$

(c): Energy of scattered electron = Energy lost by photon

Thus, difference of initial and final energies of photon is the energy of scattered electron.

$$\Rightarrow E_{\text{electron}} = \frac{hc}{\lambda_{\text{initial}}} - \frac{hc}{\lambda_{\text{final}}}$$
$$= hc \left(\frac{1}{\lambda_{\text{initial}}} - \frac{1}{\lambda_{\text{final}}}\right)$$

=
$$6.63 \times 10^{-34} \times 3 \times 10^{8} \left(\frac{1}{1.4 \times 10^{-10}} - \frac{1}{2.8 \times 10^{-10}} \right)$$

= 7.10×10^{-16} J

EXAM DATES 2016

1st May **AIPMT**

4th & 5th May Karnataka CET

5th Mav MHT-CET

8th May COMED K

14th & 15th May J & K CET

14th to 28th May **BITSAT**

17th May **WB JEE**

22nd Mav JEE Advanced

29th Mav **AIIMS**

1st June

AMU (Med.)

5th June **JIPMER**

6. (d): For case I, heat produced can be exchanged with surroundings due to slow process and hence, the change is isothermal *i.e.*; $\Delta T = 0$.

For case II, the change is adiabatic.

Thus,
$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

 $300 \times V^{(1.4-1)} = T_2 \times \left(\frac{V}{2}\right)^{(1.4-1)}$
 $300 \times (2)^{(0.4)} = T_2$
 $\log 300 + 0.4 \log 2 = \log T_2$
 $2.477 + 0.120 = \log T_2$
 $2.597 = \log T_2$
 $T_2 = \text{Antilog } (2.597) = 395.36 \text{ K}$
Change in temperature $(\Delta T) = T_2 - T_1$

7. (a): Number of oxygen atoms in a unit cell arranged in *hcp* arrangement is 12.

Contribution of oxygen atoms per unit cell

$$=12\times\frac{1}{2}=6$$
 atoms

Number of tetrahedral voids = $2 \times no$. of oxygen atoms per unit cell

$$=2\times 6=12$$

Number of metal (*M*) atoms = $12 \times \frac{2}{3} = 8$ atoms

Thus, in a unit cell, there are 8 M atoms and 6 oxygen atoms.

Simple ratio of no. of M and O atoms = 8 : 6

Hence, formula of the compound is M_4O_3 .

8. (a):
$$r_{\text{atom}} = \frac{\sqrt{3}}{4}a$$
; Also, closest approach in *bcc*

lattice is
$$\frac{1}{2}$$
 of body diagonal, *i.e.*, $\frac{\sqrt{3}}{2}a = 1.73 \text{ Å}$

or
$$a = \frac{1.73 \times 2}{\sqrt{3}} = 1.997 \text{ Å} = 199.7 \text{ pm} \approx 200 \text{ pm}$$

9. (3):

These three carbocations will give three different substituted alcohols.

10. (8): Percentage ionic character

=
$$\frac{\text{Experimental value of dipole moment}}{\text{Theoretical value of dipole moment}} \times 100$$

= $\frac{1.03}{6.12} \times 100 = 16.8 \approx 17\%$

Thus,
$$x + y = 1 + 7 = 8$$



No weightage to Board examinations' marks in Entrance Exam

Class 12 board examination marks will not be taken into account for calculating ranks in the JEE Main, which is the gateway for admission into National Institutes of Technology (NITs) from the 2016-17 academic year, HRD ministry said on 7th April, 2016.

The JEE is a national common entrance examination conducted to provide admissions to several engineering courses, including the prestigious Indian Institutes of Engineering (IITs) and NITs.

According to the existing policy, 40% weightage is given to board exam marks in determining the ranks for JEE-Main score.

However, for the candidates to qualify in the JEE examination, they need to secure at least 75% marks or be in the top 20% percentile in the class 12 examination conducted by respective boards, a senior HRD official said.

For SC/ST students, this has been relaxed to 65% marks.

The weightage system was introduced in 2012 by then HRD minister Kapil Sibal in the belief that students would pay more attention to board exams instead of concentrating on the curriculum of coaching institutes. Following the delay in publishing of ranking lists, the Smriti Irani-led HRD ministry formed a panel to study the weightage system and submit its recommendations.

This is the second UPA introduced decision related to examination reforms scrapped by the NDA government. Earlier, the controversial percentile system that governed students' eligibility for admissions into the IITs was changed in September last year.

The system required successful candidates to be among the top-20 percentile scorers in the Class 12 exams of their respective boards.



Chemical Bonding and Molecular Structure, d - and f - Block Elements

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Chemical Bonding

- ☐ The process of combination of atoms, called chemical bonding involves the union of two or more atoms through redistribution of electrons to acquire minimum energy.
- □ Kossel and Lewis proposed the electronic theory of chemical bonding according to which atoms achieve stable octet when they are linked by chemical bonds.
- ☐ Atoms combine together either by transferring or by sharing of valence electrons.
- ☐ The attainment of noble gas configuration $ns^2 np^6$, in the valence shell is the driving force behind the formation of chemical bonds.
- ☐ There are mainly three types of bonds :
 - (i) Ionic bond,
- (ii) Covalent bond
- (iii) Coordinate bond

Ionic Bond

- ☐ The bonds formed between atoms by transferring of valence electrons from one atom to another is said to be electrovalent or ionic bond, and the compound so formed is an ionic compound.
- □ Conditions for the formation of electrovalent bond:
 - Number of valence electrons: The atom which changes to a cation must contain 1, 2 or 3 electrons and the one changing to anion must contain 5, 6 or 7 valence electrons.
 - *Electronegativity difference*: Higher the electronegativity difference between the atoms, more ionic will be the bond formed.
 - Low ionisation energy: Ionisation energy of the element forming the cation *i.e.*, metal, should be low.
 - *High electron affinity*: Electron affinity of the element forming anion *i.e.*, non-metal, should be high.

• *High lattice energy*: Higher the lattice energy, greater is the ease of formation of ionic compound.

Covalent Bond

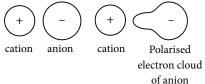
Bond formed by sharing of electrons between the combining atoms is called covalent bond and the compound so formed is a covalent compound.

Coordinate Bond

☐ A covalent bond in which both electrons of the shared pair are contributed by one of the atoms only, is called a coordinate bond or dative bond and the compound is called a coordinate compound.

Polarisation

□ Fajan's rule: In ionic bond, some covalent character is introduced because of the tendency of the cation to polarise the anion. In fact, cation attracts the electron cloud of the anion and pulls electron density between two nuclei.



According to Fajan's rule:

- Smaller the size of cation, larger is its polarising power.
- Larger the size of anion, more will be its polarisability.
- More the charge on cation and anion, more is the covalent character.
- O Cations having 18 electrons in outermost shell bring greater polarisation than the other which have 8 electrons in outermost shell.

Bond Parameters

- **Bond length:** It is the distance between the nuclei of two bonded atoms in a molecule.
 - Covalent radius: It is the radius of the core of an atom in contact with the core of an adjacent atom in a bonded situation.

- van der Waals radius: It is half the distance between two similar adjacent atoms belonging to two nearest neighbouring molecules of the same substance in solid state.
- **Bond angle**: It is the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion.
- **Bond enthalpy:** It is the amount of energy required to break one mole of bonds of a particular type between the two atoms in the gaseous state.
- **Bond order:** It is the number of bonds between the two atoms in a molecule.

Hydrogen Bonding

☐ It is the force of attraction that exists between the hydrogen atom covalently bonded to highly electronegative atom (N or F or O) in a molecule and the electronegative atom of the same or neighbouring molecule. The bond is represented by a dotted line as shown below:

☐ The hydrogen bond is of two types, intermolecular (formed between H-atom of one molecule and electronegative atom of neighbouring molecule) and intramolecular hydrogen bond (formed between H-atom and electronegative atom of the same molecule).

Valence Shell Electron Pair Repulsion Theory (VSEPR)

■ Postulates of the theory are as follows :

- Shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.
- Electron pairs in the valence shell repel one another and the order of repulsion is:

$$lp - lp > lp - bp > bp - bp$$

Electron pairs tend to occupy such positions in space that minimises repulsion and maximises the distance between them.

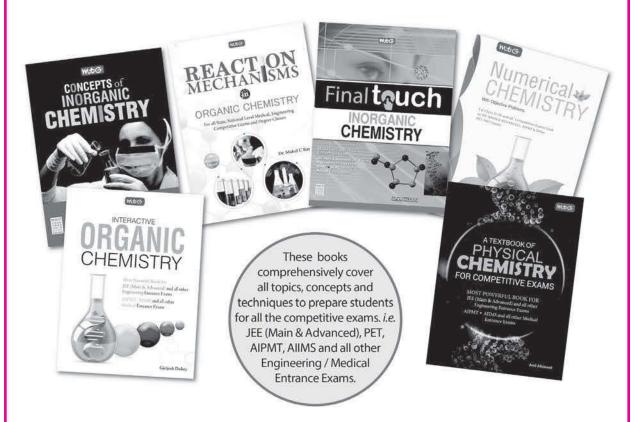
Hybridisation (Valence Bond Approach)

- The process of mixing of atomic orbitals of nearly same energy to produce a set of entirely new orbitals of equivalent energy and same shape is known as hybridisation.
- The features of hybridisation are as follows:
 - Number of hybrid orbitals = Number of atomic orbitals undergoing hybridisation.
 - Hybrid orbitals are always equivalent in energy and shape.
 - Hybrid orbitals are more effective in forming stable bonds.
 - O Hybrid orbitals are directed in space in preferred direction to have minimum repulsions between electron pairs and thus, from a stable arrangement. Hence, the type of hybridisation indicates the geometry of the molecules.

	Shapes of some simple molecules										
Type of molecule	No. of bond pairs	No. of lone pairs	Total no. of electron pairs	Type of hybridisation involved	Geometry of molecules	Examples					
AB_2	2	0	2	sp	Linear	BeF ₂ , [Ag(NH ₃) ₂] ⁺					
AB_3	3	0	3	sp^2	Trigonal planar	BF ₃ , BCl ₃					
AB_2L	2	1	3	sp^2	Bent or V-shaped	SnCl ₂ , PbCl ₂					
AB_4	4	0	4	sp^3	Tetrahedral	CH ₄ , SiF ₄ , CCl ₄					
AB_3L	3	1	4	sp ³	Trigonal pyramidal	NH_3 , PX_3 ($X = F$, Cl , Br , I)					
AB_2L_2	2	2	4	sp ³	Bent or V-shaped	H ₂ O, OF ₂ , SCl ₂					
AB_5	5	0	5	sp³d	Trigonal bipyramidal	PF ₅ , PCl ₅ , SbCl ₅					
AB_4L	4	1	5	sp³d	See-saw	SF ₄ , TeBr ₄					
AB_3L_2	3	2	5	sp³d	T-shaped	ClF ₃ , XeOF ₂					
AB_2L_3	2	3	5	sp ³ d	Linear	XeF ₂ , ICl ₂ ⁻ , I ₃ ⁻					
AB_6	6	0	6	sp^3d^2	Octahedral	SF ₆ , [SbF ₆] ⁻					
AB_5L	5	1	6	sp^3d^2	Square pyramidal	IF ₅ , ClF ₅ , BrF ₅					
AB_4L_2	4	2	6	sp^2d^3	Square planar	XeF ₄ , ICl ₄					
AB_7	7	0	7	sp^3d^3	Pentagonal bipyramidal	IF ₇ , XeF ₆					



Master Resource Books in Chemistry



HIGHLIGHTS:

- Concise theory for competitive exams
- Illustrations with detailed solutions
- Twists and turns to learn important formulae
- Elaborate solutions to mysterious NCERT problems
- · Practice assignments with pinch of hints
- Solved MCQs single and multiple option correct type, Assertion & Reason, Fill in the blanks, True or False, Comprehension, Integer & Matching types with Miscellaneous Questions

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Molecular Orbital Theory

- □ According to this theory, all the atomic orbitals of the atoms participating in molecule formation get disturbed when the concerned nuclei approach nearer. They all get mixed up to give rise to an equivalent number of new orbitals that belong to the molecule now. These are called molecular orbitals.
- When two atomic orbitals overlap they can be in phase (added) or out of phase (subtracted). If they overlap in phase, constructive interference occurs and probability of finding the electrons in the region between two nuclei increases and a bonding molecular orbital is produced.
- ☐ When two atomic orbitals overlap out of phase, destructive interference reduces the probability of finding an electron in the region between the nuclei and antibonding molecular orbital is formed.
- The order of energy is as follows:
 - Antibonding M.O. > A.O. combining > Bonding
 - For diatomic homonuclear molecules such as Li₂, Be₂, B₂, C₂, N₂, order of energy of molecular orbitals is

$$\sigma ls, \sigma^* ls, \sigma 2s, \sigma^* 2s, \frac{\pi^2 p_x}{\pi^2 p_y}, \sigma^2 p_z, \frac{\pi^* 2 p_x}{\pi^* 2 p_y}, \sigma^* 2 p_z$$

For homonuclear diatomic molecules such as O2, F2, Ne2, order of energy of molecular orbitals is

$$\sigma$$
ls, σ * ls, σ 2s, σ * 2s, σ 2 p_z , σ 2 p_z , σ 4 p_z , σ 5 p_z , σ 5 p_z , σ 5 p_z

Energy increases d- AND f - BLOCK ELEMENTS

d - Block Elements

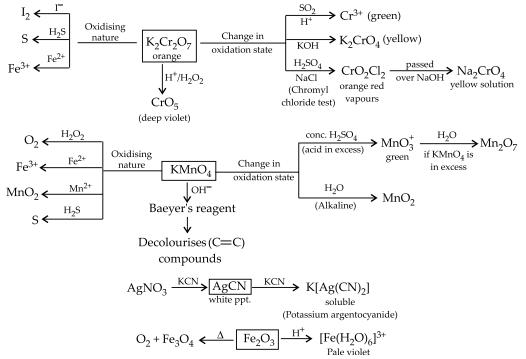
The *d*-block elements are also called as transition elements because their properties lie in between those of s-block and p-block elements and represent a transition from them. These elements are called d-block elements since in them 3d, 4d, 5d and 6d subshells are incomplete and the last electron enters the (n-1)d orbitals, *i.e.*, penultimate shell. Their general electronic configuration is $(n-1)d^{1-10} ns^{0-2}$ where *n* is the outermost shell.

Series	Elements
First transition series or 3 <i>d</i> series	Sc (At. no. 21) to Zn (At. no. 30)
Second transition series or 4 <i>d</i> series	Y (At. no. 39) to Cd (At. no. 48)
Third transition series or 5 <i>d</i> series	La (At. no. 57), Hf (At. no. 72) to Hg (At. no. 80)
Fourth transition series or 6 <i>d</i> series	Ac (At. no. 89), Rf (At. no. 104) to Uub (At. no. 112)

Some important compounds of *d*-block elements

Compounds	Preparation	Physical properties	Uses				
K ₂ Cr ₂ O ₇	From sodium dichromate (obtained from chromite ore) $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$	Orange red, crystalline solid, oxidising agent, melting point = 669 K	In dyeing, photography, leather industry				
KMnO ₄	From potassium manganate $2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$	Dark violet, crystalline solid, oxidising agent, melting point = 513 K	Baeyer's reagent (alkaline				
CuSO ₄ ·5H ₂ O (Blue vitriol)	From cupric oxide $CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$	Blue (hydrated salt), at 403 K becomes anhydrous, readily dissolves in water					
AgNO ₃ (Lunar caustic)	From silver metal $3Ag + 4HNO_3 \longrightarrow 3AgNO_3 + NO\uparrow + 2H_2O$	White crystalline, decomposes to give silver at high temperature					
HgI_2	From mercuric chloride $HgCl_2 + 2KI \longrightarrow HgI_2 + 2KCl$	It exists in two forms, <i>i.e.</i> , red and yellow, dissolves in excess of KI to form a complex, called as Nessler's reagent	for making ointments for				

Some important reactions

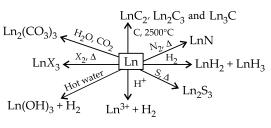


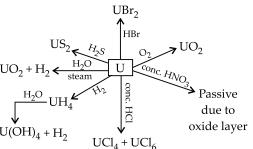
f- Block Elements

- The general electronic configuration of the *f*-block elements is $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.
- \square For lanthanoids, n is 6 while its value is 7 for actinoid series.

Lanthanoids	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
Actinoids	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

- ☐ Elements with atomic number greater than 92 (atomic number of uranium) are called transuranium elements. All these elements are man-made.
- □ Lanthanoid contraction: In lanthanoids, there is progressive decrease in atomic and ionic radii with increase in atomic number from La to Lu. This regular decrease is known as lanthanoid contraction.
 - O Cause of lanthanoid contraction: As we move along the lanthanoid series, the nuclear charge increases by one unit at each successive element and a new electron enters the 4f-subshell. Due to the peculiar shape of f-orbitals, there is imperfect shielding of 4f-electrons by other electrons in this subshell from the nuclear attraction. As a result of this, the size of lanthanoid atoms keep on decreasing from La to Lu.





Actinoids form oxo-ions such as UO₂²⁺, PuO₂²⁺, UO⁺, UO₂⁺, etc. These ions are stable in acids and aqueous solutions while lanthanoids do not form oxo-ions.



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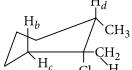
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OLYMPIAD SOLVED PROBLEMS

1. Consider a class room of dimensions $5 \times 10 \times 3 \text{ m}^3$ at temperature 20°C and pressure 1 atm. There are 50 people in the room, each loosing energy at the average of 150 watt. Assuming that the walls, ceiling, floor and furniture are perfectly insulated and none of them is absorbing heat, how much time will be needed for raising the temperature of air in the room to body temperature, *i.e.*, 37°C?

For air $C_p = \frac{7}{2}R$. (Loss of air to the outside as the temperature rises may be neglected.)

- (a) 411.3 seconds
- (b) 500 seconds
- (c) 430 seconds
- (d) 400 seconds
- 2. In the following halogen-substituted hydrocarbon, the hydrogen atom that can be eliminated most readily is H_d
 - (a) H_a
 - (b) H_b
 - (c) H_c
 - (d) H_d



3. The wave function of 2*s* electron is given by

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/a_0}$$

It has a node $r = r_0$. Then

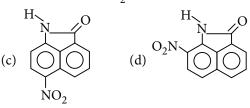
- (a) $r_0 = a_0$
- (b) $r_0 = 2a_0$
- (c) $r_0 = a_0/2$
- (d) $r_0 = 3a_0$
- 4. A dilute solution of KCl was placed between two Pt electrodes 10.0 cm apart, across which a potential difference of 6.0 volt was applied. How far would K⁺ ions move in 2 hours at 25°C?

(Given: ionic conductivity of K^+ at infinite dilution is 73.52 S cm² eq⁻¹ at 25°C.)

- (a) 4.26 cm
- (b) 3.292 cm
- (c) 5.341 cm
- (d) 2.264 cm

5. The major product of the following reaction is

$$H \longrightarrow O \xrightarrow{NO_2^+ BF_4^-} ?$$



- The spin magnetic moment of electrons in an ion is 4.84 B.M. Its total spin will be
 - $(a) \pm 1$
- (b) ± 2
- (c) ± 1.5
- (d) none of these.
- 7. Ethanol undergoes decomposition to form two sets of products:

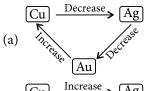
$$C_2H_5OH_{(g)} \longrightarrow C_2H_{4(g)} + H_2O_{(g)};$$

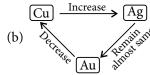
 $\Delta H^{\circ} = -45.54 \text{ kJ}$
 $C_2H_5OH_{(g)} \longrightarrow CH_3CHO_{(g)} + H_{2(g)};$
 $\Delta H^{\circ} = -68.91 \text{ kJ}$

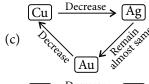
If the molar ratio of C_2H_4 to CH_3CHO in the product is 8 : 1, determine energy involved in the decomposition of 1 mole of ethanol.

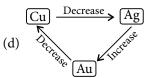
- (a) + 52.02 kJ
- (b) +48.13 kJ
- (c) -48.13 kJ
- (d) -52.02 kJ

- 8. The trade name of trichloroethylene is
 - (a) freon
- (b) westron
- (c) westrosol
- (d) DDT.
- **9.** Which systematic diagram is correct about ionisation energy of coin metals?









- 10. The K_a values for formic acid and acetic acid are 2.1×10^{-4} and 1.1×10^{-5} respectively. Calculate relative strength for formic acid to acetic acid.
 - (a) 1:1
- (b) 1:2
- (c) 4.36:1
- (d) 1:4.36
- 11. Pick up the correct statement regarding the following resonating structures of the anilinium ion :

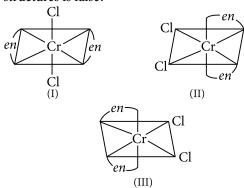
- (a) II is not acceptable because carbonium ions are less stable than ammonium ions.
- (b) II is not acceptable because it is non-aromatic.
- (c) II is not acceptable because here nitrogen has 10 valence electrons.
- (d) II is an acceptable canonical structure.
- 12. Consider the reaction,

$$(NH_4)_2HAsO_3 + CuSO_4 \longrightarrow \underbrace{CuHAsO_3}_{Green ppt.} + (NH_4)_2SO_4$$

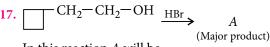
The green precipitate is also known as

- (a) Paris green
- (b) Scheele's green
- (c) Verdigris' green
- (d) Rinmann's green.

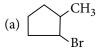
- 13. 1.00 g of $Cr_2O_7^{2-}$ is oxidised in an acidic solution by an excess of SO_2 to form HSO_4^{-} and Cr^{3+} ions. What is the minimum number of moles of H^+ that must be produced for this reaction to occur $(Cr_2O_7^{2-} = 216)$?
 - (a) 0.0231
- (b) 0.0282
- (c) 0.0322
- (d) 0.0268
- **14.** Extraction of Ag from sulphide ore and removal of unreacted silver bromide from photographic plate involve complexes
 - (a) $[Ag(S_2O_3)_2]^{3-}$ in both
 - (b) $[Ag(CN)_2]^-$ in both
 - (c) $[Ag(S_2O_3)_2]^{3-}$, $[Ag(CN)_2]^{-}$ respectively
 - (d) $[Ag(CN)_2]^-$, $[Ag(S_2O_3)_2]^{3-}$ respectively.
- **15.** Which of the statements about the following structures is false?

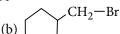


- (a) I and either II or III are *trans* and *cis*-isomers.
- (b) I and II are enantiomers.
- (c) II and III are optical isomers.
- (d) I, II and III are isomers.
- **16.** The radius of a soap bubble is 5 cm. The surface tension of the soap film is 3.5×10^{-2} N m⁻¹. What is the work done in blowing the bubble?
 - (a) 4.4×10^{-2} J
- (b) 1.1×10^{-2} J
- (c) 1.1×10^{-3} J
- (d) 2.2×10^{-2} J



In this reaction *A* will be







(d) Rr

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- 18. Which of the following is a correct statement?
 - (a) In less acidic solution, K₂Cr₂O₇ and H₂O₂ give violet coloured diamagnetic $[CrO(O_2)(OH)]^-$ ion.
 - (b) In alkaline H₂O₂, K₃CrO₈ (with tetraperoxo species) $[Cr(O_2)_4]^{3-}$ is formed.
 - (c) In ammoniacal solution, K2Cr2O7 gives $(NH_3)_3CrO_4$.
 - (d) All of these
- 19. The oxidation potentials of H-electrodes set up in buffer solution of a weak acid HX and its salt NaX in the mole ratios of x : y and y : x are E_1 and E_2 volts respectively at 25°C. The pK_a value of the acid at 25°C is
 - (a) $\frac{E_1 + E_2}{0.059}$ (c) $\frac{E_2 E_1}{0.118}$
- (b) $\frac{E_1 E_2}{0.118}$ (d) $\frac{E_1 + E_2}{0.118}$

- **20.** Which of the following compounds is not coloured?
 - (a) Na₂[CuCl₄]
- (b) Na₂[CdCl₄]
- (c) $Fe_4[Fe(CN)_6]_3$
- (d) None of these

21.
$$\bigcirc + CH_3 - CH_2 - SH \longrightarrow A$$

Identify (A) in the above reaction.

22. For a consecutive reaction,

$$R_1 \xrightarrow{k_1} R_2 \xrightarrow{k_2} R_3$$

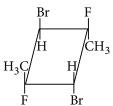
if initial concentration of R_1 is 100 M, and

 $k_1 : k_2 = 1.0 : 0.15$, the value of $[t]_{\text{max}}$ is

[Given : $k_1 = 4.0 \times 10^{-2} \text{ min}^{-1}$]

- (a) 80.55 min
- (b) 55.80 min
- (c) 58.50 min
- (d) 85.0 min
- 23. One of the hazards of nuclear explosion is the generation of 90Sr and its subsequent incorporation in bones. This nucleide has a half life of 28.1 years. Suppose one microgram was absorbed

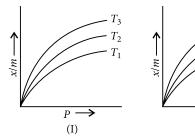
- by a new-born child, how much 90Sr will remain in his bones after 20 years?
- (a) 6.1×10^{-7} g (c) 6.1×10^{-8} g
- (b) 5.2×10^{-4} g
- (d) 5.2×10^{-5} g
- 24. The given compound has



- (a) plane of symmetry
- (b) axis of symmetry

(II)

- (c) centre of symmetry
- (d) no symmetry.
- 25. Two sets of adsorption isotherms I and II for N₂ and O2 respectively are shown in the figure. If wood charcoal is the adsorbent, the correct order of temperatures will be

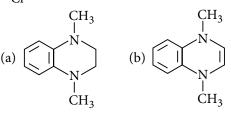


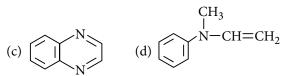
- (a) $T_1 > T_2 > T_3$; $T_1' > T_2' > T_3'$ (b) $T_1 < T_2 < T_3$; $T_1' < T_2' < T_3'$ (c) $T_1 > T_2 > T_3$; $T_1' < T_2' < T_3'$ (d) $T_1 < T_2 < T_3$; $T_1' > T_2' > T_3'$

- **26.** Identify 'A' in the given reaction,

$$\begin{array}{c}
CH_3 \\
N-CH_2-CH_2-N-CH_3 \xrightarrow{NaNH_2} A'
\end{array}$$

$$\begin{array}{c}
H
\end{array}$$





- 27. Cl₂ gas is passed into aqueous solution of KBr and KI and CHCl₃ added. It is observed that there is
 - (a) violet colour in CHCl₃ layer
 - (b) yellow colour in CHCl₃ layer
 - (c) yellow colour in aqueous layer
 - (d) violet colour in KI layer.
- 28. When an electron in an excited atom falls from L to K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75° by plane with a separation of 2.64 Å. The difference in energy between K-shell and L-shell in the atom is given by [assuming a first order diffraction $(\sin 7.75 = 0.1349)]$

(a)
$$\frac{6.62 \times 10^{-34} \times 3 \times 10^{10}}{0.7123 \times 10^{-10}}$$
 (b)
$$\frac{6.62 \times 3 \times 10^{-16}}{0.7123}$$

(c)
$$\frac{0.7123}{6.62 \times 3} \times 10^{14}$$
 (d)

29. A compound 'X' discharges bromine water in CCl₄. The compound does not give effervescence of CO₂ with aq. NaHCO₃ solution. However, its hydrolysate with conc. KOH followed by acidification gives another compound 'Y' which gives colour with FeCl₃ solution as well as effervescences of CO₂ with NaHCO₃ solution. Compounds X and Y respectively

(a)
$$CH=CHCOOCH_3$$
 and OCH_3 $CH=CHCOOH$

(c)
$$\bigcirc$$
 and \bigcirc OH

30. In the following reaction sequence,

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} NaBO_2 + (A) + H_2O$$

 $(A) + MnO \xrightarrow{\Delta} (B)$

- (A) and (B) respectively are
- (a) Na_3BO_3 and $Mn_3(BO_3)_2$
- (b) $Na_2(BO_2)_2$ and $Mn(BO_2)_2$
- (c) B_2O_3 and $Mn(BO_2)_2$
- (d) none of these.

ANSWER KEYS

- (a) (b) (b) (c) 4.
- (b) (c) 8. (c) 9. (d) **10.** (c)
- **11.** (c) **12.** (b) 13. (a) **14.** (d) **15.** (b)
- **16.** (d) 17. (a) 18. (d) **19.** (d) **20.** (b)
- **21.** (c) 22. (b) (a) (c) **25.** (c) 23.
- **26.** (a) (a) (b) (c)

SOLUTIONS OF APRIL 2016 CROSSWORD

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							⁷ C							L			L		N			Т		С
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13 F							С					¹⁴ A	N	T	I	K	N	0	С	K				N
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Do you have a question that you just can't get answered?

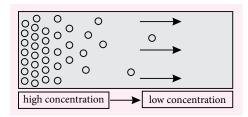
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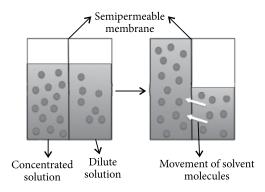
Q1. In diffusion, the molecules go from denser to rarer solution but in osmosis the flow of molecules follow just the opposite pathway. Why does it happen?

(Taniya Mondal, West Bengal)

Ans. Diffusion is the migration of matter down the concentration gradient *i.e.*, matter migrates from the region of its higher concentration to the region of its lower concentration.



Osmosis is however, defined as the flow of solvent molecules only, from less concentrated solution (high concentration of solvent molecules) to more concentrated solution (low concentration of solvent molecules).



In osmosis, semipermeable membrane does not allow the solute molecules to pass through it. Thus, osmosis is not the opposite of diffusion but it is just the special case of diffusion in which only solvent molecules migrate from higher density region to lower density region.

Q2. The *d-d* transition is absent in mercury compounds but still some mercury compounds like cinnabar and many other are coloured. Why?

(Pinaki Chattopadhyay)

Ans. Most of the times the reason behind the colour of compounds of transition elements is d-d transition but when it is not possible such as in case of mercury then the another main reason is charge transfer. Charge can be transferred either from ligand to metal or from metal to ligand. In case of cinnabar (HgS), the colour arises due to ligand to metal charge transfer. This charge transfer occurs due to relatively high energy lone pairs that are available on ligand S and the mercury metal has low-lying empty orbital. In HgS, there exist Hg²⁺ and S²⁻ ions, thus the lone pair available as π -electrons on S²⁻ gets transferred to the empty 6s-orbital of Hg²⁺ ion [Hg²⁺ (6s) \leftarrow S²⁻ (3p)] which imparts red colour to cinnabar.

Q3. Carbon generally has valency four but in carbon monoxide it is two. Why?

(Arman Ameen)

Ans. Valency of an element is the number of valence electrons involved in bonding with other elements. In case of compounds like CH₄, CO₂ etc., carbon forms four bonds by sharing its four electrons with other elements while in the case of CO, the bonding is explained as follows:

Here, out of four valence electrons of carbon only two electrons are shared with oxygen to form double bond. Then to complete the octet, the lone pair on oxygen atom is donated to carbon to form a coordinate bond and the molecule becomes stable. Here, it is clearly visible that two valence electrons on carbon atom exist as lone pair and the remaining two electrons are involved in bonding. Thus, carbon shows valency of two in carbon monoxide.



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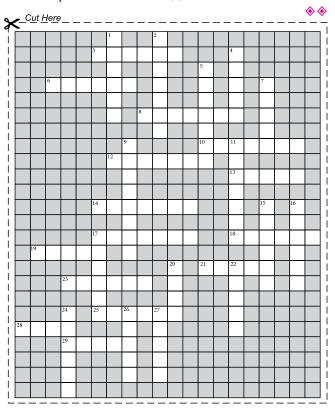
ACROSS

- 3. A volatile oil and the main constituent of lemon-grass oil. (6)
- 6. A quantum of light energy. (6)
- **8.** The amount of energy that is not available for work in a closed thermodynamic system. (7)
- 10. Trivial name of CF₃SO₃H acid. (7)
- 12. An amino acid which is abbreviated as 'Ala'. (7)
- 13. Type of mixtures for which Raoult's law is applicable. (5)
- **14.** Carbohydrate stereoisomers which differ only in configuration at the hemiacetal carbon atom. (7)
- **17.** Defect in a crystal lattice in which smaller ion (usually cation) is dislocated from its normal site to an interstitial site. (7)
- **18.** Dense form of calcium carbonate often used for decorative purpose. (6)
- **19.** A compound formed by the addition polymerisation of two molecules of a monomer. (5)
- **21.** An isotherm that relates the chemical potential at an interface and the change in surface tension. (5)
- 23. Trivial name of but-2-en-l-yl group. (6)
- **25.** Scientist who explained that in forming the solution, the salt dissociates into charged particles. (6)
- **28.** An electrical cell that produces electricity directly by the electrochemical conversion of gaseous or liquid chemicals in the cell. (4)
- **29.** A group which consists of a methylene bridge attached to vinyl group. (5)

DOWN

- 1. A pentose sugar present in all plant and animal cells. (6)
- 2. A reactive species containing a formally divalent carbon atom. (7)
- **4.** An organic chemist who won the Nobel prize for his work on retrosynthetic analysis. (5)
- **5.** A very rare carbon mineral. (7)
- Compound formed when highly electropositive metals combine with the moderately electronegative elements or metalloids or even metallic main group elements. (5)
- 9. The reserve carbohydrate of the animal cells. (8)

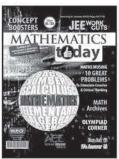
- **11.** The transition element involved in the Vaska's compound. (7)
- **15.** An equation that relates emf of a cell with the activities of the reactants and products of the cell reaction. (6)
- **16.** Type of hydrides formed when the alkali metals are heated in hydrogen. (6)
- **17.** Group of CFCs used extensively as solvents, refrigerants, blowing agents and inert dispersing agents in aerosols. (6)
- **20.** Substance used as a fuel and as a reducing agent in blast furnace. (4)
- **22.** Coherent elastic scattering of monochromatic neutrons by a set of crystal planes was explained by ______. (5)
- 24. A highly ionised gas. (6)
- **26.** A blend of metals prepared by mixing the components. (5)
- **27.** A naturally occurring sodium carbonate formed by evaporation of soda lakes. (5)



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